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First-principles investigation of an epitaxial silicon oxynitride layer on a 6*H*-SiC(0001) surface

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In a recent publication, Shirasawa *et al.* [Phys. Rev. Lett. **98**, 136105 (2007)] have experimentally shown that incorporation of nitrogen at the interface of a silicate adlayer on 6*H*-SiC(0001) leads to the formation of a well ordered, highly stable epitaxial silicon oxynitride (SiON) layer without dangling bond states. We investigate the structural and electronic properties of this intriguing system by employing density functional theory with self-interaction-corrected pseudopotentials. Our results corroborate the structural model inferred from low-energy electron diffraction. In addition, our calculated filled- and empty-state scanning tunneling microscopy images are in excellent agreement with the experimental data, clearly revealing that O and Si surface states of the silicate double layer on top of the system, respectively, give rise to the observed images. The calculated surface band structure exhibits a surface band gap of 9 eV in very good agreement with the scanning tunneling spectroscopy data. The physical origin of this amazingly large gap is clarified.

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Silicon carbide (SiC) is a material of considerable interest in experimental as well as in theoretical researches. Due to its large band gap and high thermal conductivity, SiC has paramount technological potential for power electronics operating at high voltage, high temperature, and high frequencies.[1,2] Concerning metal-oxide-semiconductor devices, ordered oxide layers on SiC surfaces have attracted particular attention. While standard preparation techniques from Si processing technology lead to interfaces with high defect densities,[3] the preparation of hexagonal SiC surfaces by hydrogen plasma or etching in hydrogen flow produces[4,5] well ordered monolayers of SiO_2. These structures, however, have one Si [C] dangling bond per unit cell at the silicate/SiC(0001) [SiC(000$\bar{1}$)] interface giving rise to undesirable interface states within the band gap.[6,7]

Very recently, Shirasawa *et al.*[8] have reported the formation of an epitaxial SiON layer on a 6*H*-SiC(0001) surface. After etching the surface in hydrogen gas and subsequent annealing at 1350 °C in nitrogen atmosphere, a $(\sqrt{3}\times\sqrt{3})R30°$ structure emerges which is unusually robust and highly stable even over a long time in air. Based on their low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements, the authors worked out a hetero-double-layer structure model for the system consisting of a silicate double layer bound to a silicon nitride double layer by straight Si-O-Si bridge bonds. The SiON layer contains five individual layers of O, Si, O, Si, and N atoms from top to bottom. This way, an atomically abrupt interface *without* dangling bonds is formed. The absence of dangling-bond-induced gap states is consistent with the scanning tunneling spectroscopy (STS) data.[8] Amazingly, the measured STS current-voltage characteristics show a band gap of about 9 eV which is mainly comparable to the bulk band gap of SiO_2 but much larger than the bulk gap (3.0 eV) of the underlying 6*H*-SiC substrate. Shirasawa *et al.*[8] referred the bright protrusions in their filled- and empty-state STM images to O and Si atoms, respectively, in the SiON layer. This interpretation was based on the density of states of *bulk* SiO_2 and Si_2N_2O due to the lack of theoretical data for the actual SiON-SiC(0001) adsorption system at hand.

In this paper, we first confirm the structural model of the system suggested in Ref. 8 and then show that the resulting electronic properties of the model explain all experimental STM and STS data[8] quantitatively. We employ density functional theory in local density approximation (DFT-LDA) to investigate the structural properties of the system. We use norm-conserving *ab initio* pseudopotentials and a basis set of atom-centered Gaussian orbitals with several shells of s,p,d, and s^* symmetry with appropriately determined decay constants.[9] The calculational method employed has been described in detail previously.[10] Here, we give only some additional information that is of particular relevance to the present system. A supercell, including the SiON adlayer, nine SiC double layers, one saturating H layer, and seven vacuum layers, is employed to describe the adsorption system. So the supercell contains 24 atomic layers in total. The surface Brillouin zone sums are carried out using 43 k points to obtain converged results. To overcome the well-known DFT-LDA limitations of the Kohn-Sham eigenvalues in describing the electronic structure, we include self-interaction corrections in the pseudopotentials yielding electronic band structures of ionic systems, in particular, in very good agreement with experiment, as shown previously.[11,12]

Most recently, a complementary theoretical study of the silicon oxynitride system has been reported by Devynck *et al.*[13] The authors employed a plane-wave pseudopotential scheme using the Troullier-Martins norm-conserving pseudopotentials in separable form and described the epitaxial SiON overlayer on SiC(0001) by periodic 3×4 supercells containing 18 atomic layers. For the Brillouin zone sums, they use Γ-point sampling (i.e., one k point per 3×4 zone). The structural properties of the system are calculated within the generalized gradient approximation[14] of density functional theory (DFT-GGA). For an improved description of the electronic structure, the authors employ the numerically much more demanding hybrid density functional approach proposed by Perdew, Ernzerhof, and Burke,[15] in which 25% of the GGA exchange energy is replaced by the respective fraction of the Hartree-Fock exchange energy which has to be evaluated explicitly.

TABLE I. Atomic coordinates (in Å) of the structure shown in Fig. 1 resulting from the present calculations in comparison with experimental data from Ref. 8. The x, y, and z directions correspond to the $[11\bar{2}0]$, $[1\bar{1}00]$, and [0001] axes, as indicated in Fig. 1. Atoms are labeled according to Fig. 1.

		Theory			Expt		
Atom	Type	x	y	z	x	y	z
2	O	0.00	2.66	0.00	0.00	2.66	0.00
4	Si	−3.07	0.00	−0.53	−3.09	0.00	−0.50
5	Si	3.07	0.00	−0.53	3.09	0.00	−0.54
6	O	−3.07	0.00	−2.13	−3.09	0.00	−2.14
7	O	3.07	0.00	−2.13	3.09	0.00	−2.16
8	Si	−3.07	0.00	−3.74	−3.09	0.00	−3.74
9	Si	3.07	0.00	−3.74	3.09	0.00	−3.74
10	N	0.00	2.13	−4.32	0.00	2.15	−4.35

We optimize the atomic structure of the $(\sqrt{3}\times\sqrt{3})R30°$ model of the SiON layer on SiC(0001) without imposing any symmetry restrictions. The final lattice configuration has C_{3v} symmetry. The calculated atomic coordinates are listed in Table I together with the LEED data from Ref. 8. The corresponding bond lengths and bond angles resulting from the calculated atomic positions are given in Table II for convenience, as well.[16] Figure 1 shows a top and a side view of the calculated structure. The adsorbed SiON film consists of five individual layers. In each $(\sqrt{3}\times\sqrt{3})R30°$ unit cell, there are three O atoms (1-3) in the topmost, two Si atoms (4,5) in the second, two O atoms (6,7) in the third, two Si atoms (8,9) in the fourth, and three N atoms (10-12) in the fifth layer. Each O atom in the first and third layers is bound to two Si atoms. All Si atoms in the SiON layer are fourfold coordinated. Each N atom binds to two Si atoms on the fourth layer and one Si atom on the top layer of the SiC substrate. These threefold coordinated N atoms are completely saturated as all other atoms in the system. Therefore, no dangling bonds exist. The calculated atomic structure is in excellent agreement with the structural model worked out by Shirasawa *et al.*[8] from their best fit to the LEED data. The latter shows only marginal deviations from the C_{3v} symmetry of the system (see Table I).

In the top silicate double layer, all Si-O pairs have the same bond length of 1.62 Å which is close to the mean Si-O bond length of 1.61 Å in α quartz. The same holds for the Si-O-Si bond angle which is 142° in the SiON layer and 144° in α quartz. Linear Si-O-Si bridges per unit cell with bond lengths of 1.60 and 1.61 Å connect the silicate double layer with the silicon nitride double layer. This way, the Si atoms in the second as well as in the fourth layer of the SiON overlayer are tetrahedrally coordinated with O-Si-O and O-Si-N bond angles of about 109°, respectively. The angular Si-N-Si bonds in the silicon nitride double layer have an angle of 126° and a bond length of 1.73 Å. These values differ only slightly from those of the Si-N bonds with Si atoms on the sixth layer having a bond angle of 113° and a bond length of 1.76 Å. The Si-N-Si bond angle of 119°, reported in Ref. 8, corresponds to the average of the two above angles. For further reference, we note that the mean Si-N-Si bond angle and the mean Si-N bond length in bulk $\alpha-Si_3N_4$ are 119° and 1.74 Å, respectively.

Interestingly, the three topmost layers of this structural model have the same Si_2O_5 configuration in each unit cell as found previously for the silicate-covered SiC(0001) surface in experiment[4,5] and theory.[7] In the latter model, however, there are *three* Si atoms in the fourth and three C atoms in the fifth layer per unit cell so that one of the three Si atoms is not fully saturated and one dangling bond per unit cell occurs.

The surface electronic spectrum of the epitaxial SiON layer on SiC(0001), as measured by STS,[8] exhibits a very large band gap of about 9 eV. In order to shed light on its physical origin, we calculate the surface band structure and local densities of states. To overcome the DFT-LDA band gap problem, we employ our self-interaction-corrected pseudopotentials.[12] Within this framework, we obtain a band gap of 3.1 eV for 6H-SiC, very close to the experimental

TABLE II. Calculated bond lengths (in Å) and bond angles (in deg) of the SiON layer. Atoms are labeled according to Fig. 1.

Straight bonds		Bond length	Angular bonds		Bond angle
4-1	Si–O	1.62	4-2-5	Si–O–Si	142
4-6	Si–O	1.60	4-6-8	Si–O–Si	180
8-6	Si–O	1.61	8-10-9	Si–N–Si	126
8-10	Si–N	1.73	8-10-13	Si–N–Si	113
13-10	Si–N	1.76			

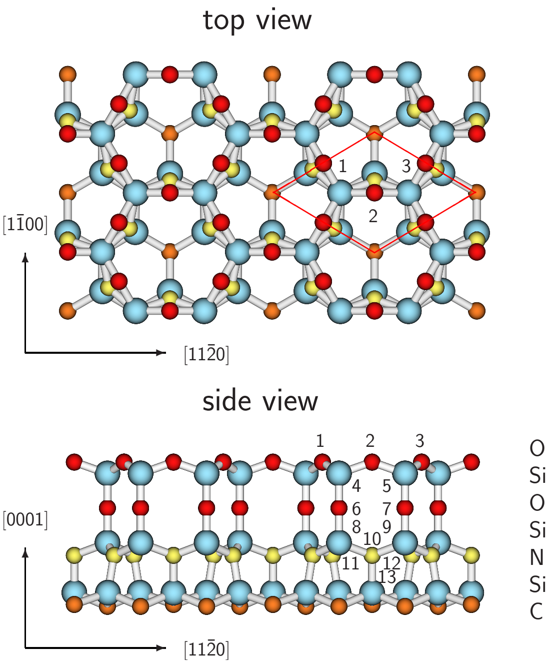

FIG. 1. (Color online) Top and side views of the SiON layer on 6H-SiC(0001), as calculated. The $(\sqrt{3}\times\sqrt{3})R30°$ surface unit cell is indicated by the red (black) diamond in the top view. O, N, and C atoms are shown by small red (black), yellow (light gray), and brown (dark gray) balls, respectively. Si atoms are depicted by large blue (light gray) balls. The numbers label the atoms on the first five layers of the unit cell and one Si atom on the sixth layer.

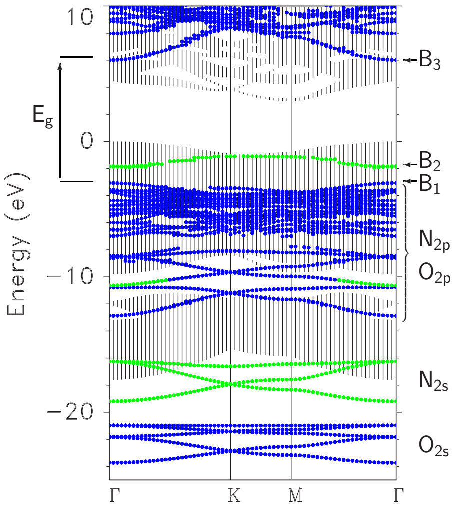

FIG. 2. (Color online) Surface band structure of a SiON layer on 6H-SiC(0001)-$(\sqrt{3}\times\sqrt{3})R30°$. The shaded area represents the (0001) projected bulk band structure of 6H-SiC. Blue (black) dotted lines indicate oxygen-derived bands, while green (gray) dotted lines indicate nitrogen-derived bands. E_g labels the surface gap of 9 eV (see text).

value of 3.0 eV. For α-SiO$_2$, our calculated band gap is 8.9 eV comparing favorably with the experimental value of 8.9 eV reported for polycrystalline[17] SiO$_2$.

The calculated surface band structure for the SiON layer on SiC(0001) is shown in Fig. 2. All bands plotted in the figure as dotted lines are related to surface bound states or resonances that stem from the SiON layer. Oxygen- and nitrogen-derived bands are shown in blue (black) and green (gray), respectively. We have labeled groups of bands according to the composition of their wave functions as O_{2s}, N_{2s}, O_{2p}, and N_{2p}, respectively. Most of these bands have also contributions from Si states localized on the second, fourth, or sixth layer. The 2s states of the five O atoms per unit cell give rise to the five O_{2s} bands between −21 and −24 eV. At the bottom of the projected SiC bulk bands between −16 and −19 eV, there exist three bands derived from N 2s states. The bound states in the ionic gap, as well as the resonances between −3 and −13 eV, stem from Si 3s and 3p, as well as O 2p and N 2p orbitals, in the SiON layer.

As noted above, all bonds in the SiON layer as well as all former dangling bonds on the clean SiC(0001) surface are fully saturated in the optimized lattice configuration. Therefore, the fundamental gap is free from surface states. Obviously, the smallest one-particle excitation energy of this system is given by the size of the substrate band gap of 3.1 eV. However, the surface related gap probed in STS experiments is mainly determined by the highest occupied and lowest unoccupied surface states that have a noticeable probability density at and above the surface. The *occupied* surface state band B_1 is formed by O 2p orbitals localized at the O atoms in the top layer. These orbitals lie in the surface plane and are perpendicular to the Si-O-Si bonds forming the hexagonal rings in the top double layer. The left panel of Fig. 3 shows the charge density of B_1 at the Γ point in a plane containing O atom 2 (see Fig. 1). The states forming the *empty* surface state band B_3 mainly extend around the Si atoms of the second layer and are localized to some extent at the O atoms in the first and third layers (see right panel of Fig. 3). The calculated band gap between states B_1 and B_3 at Γ is 9 eV. These states are directly accessible in STS. Therefore, the direct surface band gap of about 9 eV, measured in STS, originates from the B_1 and B_3 states at Γ. We note in passing that surface state band B_2 is predominantly formed by N 2p orbitals localized on the fifth layer. Therefore, these states do not contribute to the STS spectrum.

To further highlight the origin of the gap measured in STS, we show in the top panel of Fig. 4 the local density of states (LDOS) $N(E,z)$ for $z=0.5$ Å above the surface in comparison with the bulklike LDOS for a z value in the middle of the slab.[18] Between −3 and +6 eV, there are practically no contributions to $N(E,z=0.5$ Å$)$ due to the fact that all states

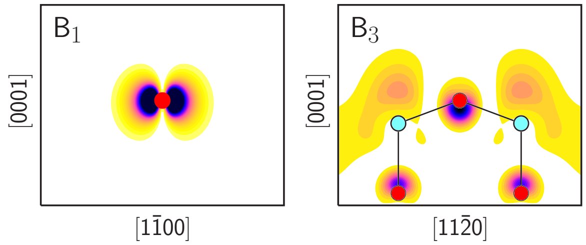

FIG. 3. (Color online) Charge-density distributions of the B_1 (left panel) and B_3 (right panel) states at the Γ point of the surface Brillouin zone. Regions of the highest and lowest charge densities are shown in black (dark gray) and yellow (light gray), respectively.

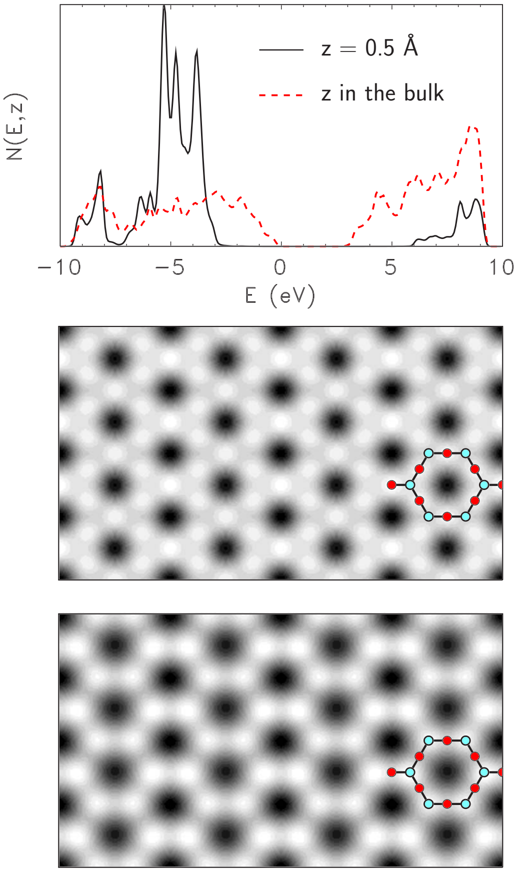

FIG. 4. (Color online) Local density of states $N(E,z)$ for $z = 0.5$ Å above the topmost O atoms of the SiON layer shown by the full black line (top panel). The red dashed line shows the bulklike LDOS for z in the middle of the slab. The filled- (middle panel) and empty-state (bottom panel) STM images are calculated in constant current mode at −3 and 6 eV, respectively. A ball and stick model for the O (filled circles) and Si (open circles) atoms in the silicate double layer is overlaid for comparison.

in this energy region have almost vanishing wave functions above the top of the SiON layer. In light of these results, the appearance of a gap of about 9 eV in the STS data[8] becomes immediately intelligible. In particular, our calculations reveal that the thin siloxane film consisting of the topmost four layers in the SiON layer gives rise to virtually the same gap as a SiO_2 crystal. This is further corroborated by a calculation for a freestanding siloxane double layer (Si_4O_8) for which we obtain a band gap of 8.6 eV.

Shirasawa *et al.*[8] have attributed the bright protrusions in their filled-state STM image to O and those in the empty-state image to Si atoms. This interpretation is fully confirmed by our results. Employing the Tersoff-Hamann approach,[19] we have calculated constant current mode filled- and empty-state STM images at −3 and +6 eV, respectively, which are shown in the middle and bottom panels of Fig. 4. The intensity maxima in the filled-state image mainly result from B_1 states whose wave functions are localized at the top layer O atoms (see left panel of Fig. 3). The spots of high intensity in the empty-state image stem from B_3 states whose wave functions are more extended above the Si than above the O atoms of the top silicate double layer (see right panel of Fig. 3). As a result, for distances z larger than 1 Å above the surface, the contributions of the Si atoms dominate the empty-state image. Comparing the calculated STM images in Fig. 4 with the respective measured images (Fig. 4 in Ref. 8) reveals that our results describe the measured topograms quantitatively.

Comparing the results of Devynck *et al.*[13] with our results and with experiment[8] reveals that both calculations yield bond lengths and bond angles of the SiON overlayer on SiC(0001) in very good mutual accord and in excellent agreement with the experimental values. Thus, the two independent *ab initio* calculations fully confirm the structural model worked out by Shirasawa *et al.*[8] on the basis of their experimental data. The different methodologies employed in our work and in Ref. 13 to evaluate the electronic structure, on the other hand, give rise to some differences. For bulk 6*H*-SiC and SiO_2, we obtain band gaps of 3.1 eV (3.0 eV) and 8.9 eV (8.9 eV), respectively, in good accord with the experimental values given in parentheses. The more demanding hybrid functional DFT-GGA calculations[13] yield 3.8 and 7.9 eV for these gaps, respectively. Likewise, our calculated surface gap of the silicon oxynitride system of 9.0 eV is in agreement with the observed[8] gap energy of about 9 eV. Devynck *et al.*[13] inferred a surface band gap of 8.1 eV for the system from the LDOS projected onto the Si and O atoms of the outermost silicate double layer. Considering the above gap values for bulk 6*H*-SiC and the overlayer system, we note that the band gap opening of 5.9 eV following from our results closely agrees with the experimental value of 6.0 eV while it results as 4.3 eV from the earlier calculation.[13] A surface band structure or charge densities of the SiON-SiC(0001) system, to which we could further compare our results, are not presented in Ref. 13. Finally, we note that the filled- and empty-state STM images reported previously[13] and our results shown in Fig. 4 are both in excellent agreement with experiment.[8]

In summary, we have shown that DFT-LDA calculations including self-interaction-corrected pseudopotentials allow for a quantitative description of structural and electronic properties of an epitaxial SiON layer on 6*H*-SiC(0001). Also, theory yields the amazingly large surface band gap of 9 eV, as observed in STS. We have clarified its physical origin. In addition, we have revealed which particular electronic states give rise to the observed filled- and empty-state STM images. Our calculated images are in very nice agreement with experiment. Future direct and inverse photoelectron spectroscopy investigations of the electronic structure reported in this work could experimentally complete the physical picture of this highly intriguing system which might well turn out to be of great technological interest for device applications.

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