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First-principles study of oxygen adsorption on the nitrogen-passivated 4*H*-SiC (0001) silicon face

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The effects of oxygen and nitrogen adsorption and interaction on the 4*H*-SiC (0001) surface are investigated using the density-functional theory coupled with molecular dynamics. Nitrogen coverages from $\frac{1}{9}$ to $\frac{5}{4}$ monolayer are considered. The adsorption sites for isolated oxygen atoms and molecules are considered as well as the interaction between oxygen and nitrogen on the surface. The primary findings are that adsorbed atomic oxygen and nitrogen repel each other. At sparse coverages ($n+m \leq \frac{1}{3}$, n=monolayers of nitrogen and m=monolayers of oxygen) the oxygen atoms bond to two surface-silicon dangling bonds while the nitrogen atoms consume three. For higher densities of oxygen and nitrogen, pairs of nitrogen atoms may combine to form N_2 dimers with each pair dangling from the top of a surface-silicon atom, thus increasing the number of silicon-surface bond sites available at the given coverage. However the N_2 are only weakly bound with respect to gas-phase N_2 and for higher coverages of oxygen, not bound at all. For equal concentrations of oxygen and nitrogen, this arrangement saturates at $\frac{2}{3}$ monolayer of nitrogen and oxygen above which coverage the N_2 is displaced by atomic oxygen. A higher-energy surface can be formed from the adsorption of NO molecules. This saturates all of the silicon-surface states at $\frac{1}{3}$ monolayer. Above this coverage a second phase consisting of N_2O_2 saturates all of the surface states at 1 monolayer and could conceivably be formed by adsorbing $\frac{1}{2}$ monolayer of N_2 onto an oxygen-saturated 4*H*-SiC silicon surface. Interestingly our study shows that the 1 monolayer coverage of NO leaves the bulk band gap free of states. This has implications for growth of nitrogen on the silicon surface in the presence of oxygen.

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I. INTRODUCTION

In recent years SiC has generated considerable interest for various electronic applications including its use as a substrate for growth of nitride films and for use in high-power and high-temperature semiconductor devices due to its wide range of advantageous physical properties.[1–3] Recently attention has been placed on studies of the interface between SiC and SiO_2 due to the poor electron field-effect mobility of this material which hinders its widespread application.[4] This is thought to arise from a high density of interface traps (D_{it}) just below the conduction-band edge.[4–11] It has been proposed that they are the result of interface defects due to carbon clusters and silicon suboxide bonds.[6,12] However existence of graphitic regions at or near the SiC/SiO_2 interface is under debate and it is possible that this is an interface phase which may be avoided.[13–15] The experimental evidence which shows that the interface states persist regardless of the method of growth suggests that they are the result of something intrinsic to the interface.[14]

A considerable amount of experimental work has shown that the introduction of N, NO, or N_2O into the interface reduces D_{it} and improves electron mobility.[2,13,15–20] Measurements on nitrogen-treated gate oxides indicate that the nitrogen coverage at the 4*H*-SiC/SiO_2 interface corresponds to $(0.35 \pm 0.13) \times 10^{15}$ and $(1.02 \pm 0.02) \times 10^{15}$ cm^{-2} or approximately $\frac{1}{3}$ monolayer (ML) and 1 ML for the silicon and carbon faces, respectively.[21] Current explanations propose that nitrogen breaks up the interface carbon clusters or passivates suboxide bonds.[22,23] However, efficient incorporation of nitrogen into the interface may be problematic since it has been found that upon reoxidation, the nitrogen concentration may be depleted or even completely removed from the interface region.[24]

Much of the theoretical work has focused on the oxidation step in processing the interface, the formation of interface defects and the mechanism involved in the nitrogen passivation of the interface defects.[8,10,25–27] Deák *et al.*[28] have conducted an extensive theoretical study of the interface between 4*H* SiC and SiO_2 to determine possible interfacial defects associated with the well-known gap states both above the valence and below the conduction-band edges. Their work employed hybrid exchange to accurately describe the positions of gap states contributed by various interfacial carbon clusters. They also described pathways for nitrogen to remove carbon clusters from the interface and either shift or remove the associated interface states away from the interface.

Less attention has been placed on theoretical studies of the SiC surface. Olander and Larsson[29,30] have looked at adsorption of nitrogen containing species and reconstruction of the surface due to the influence of adsorbed species. Recently there has also been a detailed theory/experimental investigation of the effects of oxygen, hydrogen, and water on the SiC surfaces.[31] In our own studies we recently presented a first-principles investigation of nitrogen adsorption onto the 4*H*-SiC Si surface in order to gain insight into the mechanism behind the passivation effects it contributes.[32,33] That work showed that silicon dangling bonds may account for part of the mechanism which creates states below the conduction-band edge of the silicon surface. The density of nitrogen on the surface required to passivate the surface states was coincidentally shown to be similar to the experimentally determined density of nitrogen at the interface.[21] That work, however, did not consider the effects of oxygen on the nitrogenated silicon surface which is important for considering oxide growth, for example. In other theoretical work, Jeong[34,35] has performed studies of NO adsorption on the Si(001) surface which has similarities to the silicon surface of SiC and may therefore lend insight.

In this paper we expand on our previous work by considering the adsorption of oxygen onto the nitrogenated 4*H*-SiC (0001) silicon surface. The primary goal of the paper is to understand how oxygen affects the stability of nitrogen bonding to the silicon surface. We pursue this study within our computational model by depositing oxygen onto the nitrogen-adsorbed surfaces for coverages of nitrogen between $\frac{1}{9}$ and $\frac{5}{4}$ ML.

Our main findings are that atomic oxygen and nitrogen adsorbed on the surface are more stable than molecular species composed of oxygen and nitrogen, oxygen is able to displace nitrogen by preferentially occupying silicon-surface bonds and the existence of stable NO adsorption phases on the surface. We are also able to gain some insight into nitrogen dissociation from this surface and also possible nitrogen-carbon bonding mechanisms.

The paper is outlined as follows. Section II outlines the computational method employed as well as the construction of the models used in this study. Section III reviews the main points of the nitrogen-only adsorbed surface. In Sec. IV a brief examination of oxygen on the clean silicon surface is examined. This section also examines the interaction of oxygen on the surface with a sparse coverage of nitrogen. The effects of oxygen on the $\frac{1}{3}$ ML nitrogen-adsorbed surface are discussed in detail in Sec. V. In the final two Secs. VI and VII, we examine the adsorption of oxygen onto the surface with a coverage greater than $\frac{1}{3}$ ML of nitrogen up to 1 ML and the findings of this paper are summarized.

II. COMPUTATIONAL DETAILS

All calculations in this studies are based on the density-functional theory (DFT) using gradient corrections.[36,37] For treatment of the electronic-structure problem the projector-augmented wave method was used.[38] The kinetic-energy cutoff for the plane-wave part of the wave functions was set to 30 Ry and that for the electron density to 60 Ry. Car-Parrinello-type[39] *ab initio* molecular-dynamics scheme was used for relaxation of the atomic positions. No symmetry was employed for any of the adsorption calculations. In cases where there are an odd number of electrons in the super cell, spin-polarization effects were included.

To construct the fundamental 1×1 SiC surface slab, first the bulk $1\times1\times1$ unit cell was optimized for lattice parameters and atomic positions. The 1×1 surface cell was constructed from this by adding 15 Å of vacuum to the silicon face and terminating the carbon-face dangling bond with an hydrogen atom. The hydrogen-carbon bond length was optimized with the SiC slab held at bulk values of atomic positions and lattice constants. The lowest bilayer, including the hydrogen, was frozen for all subsequent calculations. The resulting fundamental cell was translated along the (100) and (010) real-space directions to achieve the desired cell sizes for subsequent calculations.

For this work three different super cells were used depending on the coverage being investigated. The principle super cell was composed of $9-1\times1$ unit surface cells arranged in a 3×3 configuration. In some cases we have also used a super cell composed of 41×1 unit surface cells arranged in a 2×2 configuration and a super cell composed of three unit cells. For the 2×2 and 3×3 super cells we used a *k*-point mesh consisting of six *k* points along each of the surface reciprocal-space directions of the 1×1 cell. The *k*-point meshes for these two cells are commensurate and introduce no errors for comparison of total energies between cells. For the super cell composed of three unit cells we used three *k* points in each surface reciprocal-space direction. The mismatch between the two *k*-point meshes introduces an error of less than 0.007 eV per 1×1 unit. This error does not factor into our final results because the effects of the super cell are subtracted by taking the energy difference between the adsorbate cell and the corresponding clean cell or other relevant cell of the same surface configuration. For all calculations we used only one *k* point for the surface-normal direction.

We calculate adsorption energies in two ways. For comparisons between different adsorption sites at the same coverage the following formula is used:

$$E_{\mathrm{ads}}=E_0[\mathrm{surf}+\mathrm{ads}]-nE_0[\mathrm{surf}]-E_{\mathrm{ref}}[\mathrm{ads}], \tag{1}$$

where E_{ads} is the adsorption energy per surface cell for the adsorbed species, $E_0[\mathrm{surf}+\mathrm{ads}]$ is the total energy of the super cell including surface plus adsorbed species, $E_0[\mathrm{surf}]$ is the total energy of the surface with the same area and shape as the adsorbed configuration, and $E_{\mathrm{ref}}[\mathrm{ads}]$ is a reference energy for the adsorbed species. The surface may not necessarily be the clean surface. If, for example, we are interested in the binding energy of an N_2 to an oxygen-adsorbed surface, then we would use the fully relaxed surface with oxygen adsorbed onto it as our reference surface. The fractional coverage is determined by dividing the number of units of the adsorbed species within a given surface cell by the number of fundamental unit cells within the surface cell. This represents the energy per unit cell to adsorb a fraction of a monolayer of the species and so differs from the chemical potential.

In cases where we wish to compare the adsorption energies at different coverages we use the following formula:[40]

$$E_{\mathrm{ads}}=\{(E_0[\mathrm{surf}+\mathrm{ads}]-nE_0[\mathrm{surf}])/l-E_{\mathrm{ref}}[\mathrm{ads}]\}\times\chi, \tag{2}$$

where the energies are as defined above, n is the number of 1×1 surface cells needed to compose the surface cell, l is the number of adsorbed units, and χ is the coverage in fractions of a monolayer. The units are adsorbed nitrogen atoms in this paper but with this formula they could be molecules in a more general case. The derivative of this with respect to the coverage of surface-adsorbed atoms give the chemical potential. The reference energies used to make the calculations in the paper are presented in Table I.

TABLE I. The Si reference energy was that of bulk Si. The oxygen energy was the residual energy after subtracting the Si reference energy from bulk SiO_2. The N reference energy was the residual energy after subtracting the O reference energy from molecular NO.

	Energy [H]
E_0[Si]	−4.0036
E_0[SiO_2]	−438.2049
E_0[O]	−16.2567
E_0[N]	−9.8685
E_0[N_2]	−20.1153
E_0[NO]	−26.1255
E_0 [4-bilayer SiC slab]	−39.6655

We also calculate energy barriers for atoms and molecules to migrate along the surface. This is done by picking the starting point on the surface and the end point. A line segment connecting these points is divided into about 4000 increments per picosecond. The species is incremented along this line segment, which specifies one of the coordinates of the species while being free to move on the surface of a plane which is orthogonal to the line segment. The position on the plane gives the other two position coordinates of the species. All other atoms in the super cell are given freedom to relax except those on the lowest bilayer. The total energy is calculated at each increment. Since the steps are small, the species stays close to the Born-Oppenheimer surface and we can get an idea of the potential-energy surface along the path that the species follows. Reactions between gas-phase atoms or molecules and the surface-adsorbed species will present different barriers but these are not considered in this paper. The barriers determined by this method do not include thermal effects which may lower the barrier heights and are thus intended as upper bounds to the actual barriers to migration on the surface.

III. SURFACE NITROGEN ADSORPTION: A REVIEW

In our previous work we considered the issue of nitrogen adsorption on the (0001) Si surface of 4*H* SiC.[32,33] To summarize those results briefly, up to $\frac{1}{3}$ ML, for the lowest-energy surface site, the nitrogen atoms chemisorb into a central position above the surface plane and between three silicon atoms, contributing one electron to each of three half-filled surface-silicon dangling bonds. Note that this site is hollow in the sense that there is no carbon in the surface bilayer beneath the nitrogen. Hereafter we will refer to this as an h_1 region (see Fig. 1). This process continues as nitrogen atoms are adsorbed until, at $\frac{1}{3}$ ML, all the surface dangling bonds have been passivated by nitrogen atoms. Throughout this text, this surface will therefore be referred to as the passivated surface. Above this coverage there is an increase in the chemical potential. Other possible bonding sites for a nitrogen atom include the hollow site between three surface-silicon atoms but with a carbon atom in the surface bilayer which we refer to as an h_2 site, the bridge site between two surface-silicon atoms and the site on top of a surface-silicon atom.

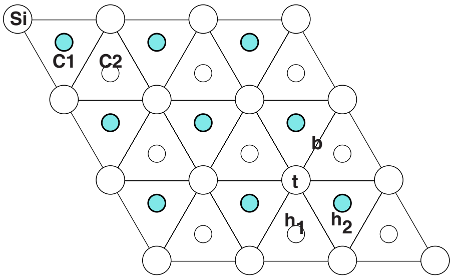

FIG. 1. (Color online) A top view schematic of the 4*H*-SiC (0001) Si surface showing the first SiC bilayer and the C atom positions in the lower layers. The atoms are as labeled in the upper right of the figure with C1 and C2 indicating the top-layer C atoms and lower-bilayer C atoms, respectively. For the purposes of this paper the surface is characterized by four surface regions labeled h_1, h_2, t and b for the two types of hollow sites, the Si top site and the bridge site between two Si atoms as labeled in the lower left of the figure.

Based on two conditions a surface phase forms in the sense that there is a regular array of adsorption atoms which should be discernible in x-ray diffraction measurements. The first is that all of the adsorption sites have a similar geometric orientation with respect to their neighbors thus forming a regular surface pattern. The second condition is that there is an increase in the chemical potential of the adsorbing species above the this coverage. Since there is an increase in the chemical potential, surface atoms do not migrate to form higher-density regions of arbitrary shape and size. This second condition is dependent on the thermodynamic conditions including the activation energy barriers, the energy barrier measured from the atoms initial position to the top of the barrier separating two local minima, for migration along the surface and kinetic energy of the migrating species on the surface. Therefore the phases represent only a low-temperature ground state and do not exclude the possibility of other surface features appearing.

Below $\frac{1}{3}$ ML all of the h_1 adsorption sites are energetically equivalent so the adsorption sites are randomly distributed. Our work showed that the chemical potential changes as the coverage goes above $\frac{1}{3}$ ML. Based on the second condition, above this coverage of nitrogen, adsorption onto the surface is less favorable so it may be possible to eliminate the excess surface nitrogen given a suitable partial pressure of nitrogen. In order for the $\frac{1}{3}$ ML phase to form either the atoms must be deposited in their ideal positions or they must migrate to those positions. The activation barrier for a nitrogen to move from an h_2 site to a low-energy h_1 site is about 0.2 eV. The highest activation barrier is about 0.7 eV for one of two nitrogens in neighboring h_1 sites to migrate away from each other, however nitrogen atoms adsorbed onto the surface tend to repel each other.

As the coverage goes above $\frac{1}{3}$ ML all non-neighboring h_1 sites are occupied. In the lowest-energy configuration, additional nitrogen atoms bond in the previously adsorbed h_1 regions forming N_2 molecules on the surface. These molecules bond to only two surface-silicon atoms, leaving an

TABLE II. The adsorption energies per atom for oxygen to adsorb onto the SiC surface relative to an isolated oxygen adsorbing on a bridge site. The table also includes the average bond lengths between the oxygen and silicon atoms. The designations nn, 2 nn, and 3 nn refer to the first, second, and third nearest-neighbor surface sites, respectively. Numbers separated by commas indicate asymmetric bond lengths. Semicolons separate bond lengths for different adatoms in the same cell. For the O_2 adsorbing intact, the oxygen bond length is in parenthesis. The calculations were performed using a collinear spin-unrestricted Hamiltonian which allows for changes in the spin configuration during the relaxation process.

Configuration	ΔE (eV/atom)	Bond length (Å)
3 nn bridge	0.00	1.78, 1.81
3 nn top	0.06	1.56
nn bridges	0.23	1.77, 1.82; 1.79, 1.80
2 nn bridge/top	0.33	1.75, 1.81/1.56
2 nn top	0.37	2×1.56
2 nn bridges	0.38	2×1.79; 2×1.80
nn top	0.53	1.56, 1.57
O_2	1.86	1.74,1.75 (1.52)

unpassivated silicon dangling bond again available and reintroducing surface states into the SiC band gap. At a coverage of 1 ML, all the Si dangling bonds are again passivated and a second phase forms. Between $\frac{1}{3}$ and 1 ML there are two types of surface regions composed of the $\frac{1}{3}$ and 1 ML coverage of nitrogen.

The above pictures requires that there are energetically accessible pathways for the formation of N_2 on the surface. An analysis of the barriers showed that nitrogen atoms on the surface are strongly repulsive and will not easily coalesce to form dimers at coverages below $\frac{1}{3}$ ML due to the mobility of the nitrogen atoms.[33] Above this coverage the mobility of the nitrogens becomes reduced due to repulsion from nearest-neighbor nitrogens. We were able drive an additional nitrogen atom into and h_1 region with a barrier to N_2 formation on the surface of about 3.7 eV. Thus N_2 is not likely to form on the surface. This suggests that as the surface concentration of nitrogen increases the surface does not spontaneously evolve from the most stable phase at $\frac{1}{3}$ ML to the most stable phase at 1 ML.

IV. LOW-COVERAGE OXYGEN AND NITROGEN ADSORPTION

We begin by determining the energetically favored adsorption sites of oxygen on the clean surface. We present our findings in Table II in which we summarize the adsorption energy per atom relative to the lowest-energy configuration for the isolated atom. We also include the bond lengths between the oxygen and the surface silicons to which they bond. Because of the periodic boundary conditions and our choice of unit-cell dimensions, single isolated oxygen atoms adsorbed onto this surface have a population density corresponding to third nearest neighbors or $\frac{1}{9}$ ML coverage.

We consider two nearest-neighbor oxygen atoms separated by two unterminated surface-silicon atoms to approximate the isolated oxygen atoms adsorbed onto the surface. In this regime, the lowest-energy adsorption site corresponds to the isolated oxygen-atom bonding in the bridge site between two silicon atoms. The oxygen p orbital is filled by the dangling electrons of the surface silicons which are therefore passivated. Lying 0.06 eV/atom higher in energy to this site a single oxygen bonds directly on top of a single silicon atom. At this adsorption site there is only a single electron available to the oxygen neglecting the possibility of electron transfer. If the oxygen is bonded to the silicon by a single valence electron then there would be an odd number of electrons in the valence p shell of the oxygen and we would expect to find a net local magnetic moment for this atom. Since we do not find a local moment on the oxygen we propose that there is some surface charge redistribution. This will be discussed in more detail later in this section. The third lowest-energy structure included in the table is for oxygens to adsorb onto two nearest-neighbor bridge sites aligned parallel to each other. A configuration with two second-nearest-neighbor bridge sites lies 0.15 eV/atom higher in energy.

The general trend is for the oxygen atoms to adsorb in such a way as to maximize their separation. This is clear for oxygen atoms adsorbed on the top sites where third nearest neighbors have the lowest adsorption energy, 0.31 eV/atom lower than for second-nearest neighbors and 0.47 eV/atom lower than for the nearest-neighbor top sites. We propose that the bridge adsorption sites are energetically favorable since they are able to bond to two surface-silicon dangling bonds thus reducing the silicon-surface energy and also closing the atomic oxygen p shell. There is a cost in surface strain, however, as the silicon atoms to which the oxygen is bonded are separated by 0.26 Å. This compares with 0.31 Å for the separation between the top-site bonded silicon and its nearest neighbor which is very similar to that of the silicon-silicon separation for the clean surface.

We have further considered the possibility of O_2 molecules adsorbing onto the surface. This configuration lies 1.63 eV/atom above the lowest-energy configuration. Depending upon the starting configuration the O_2 dissociates into oxygens adsorbed onto two different bridge sites. Therefore we conclude that molecular oxygen is not stable on this surface.

We next turn to examining the interaction between the nitrogen and oxygen on the surface. At $\frac{1}{9}$ ML the lowest-energy surface site for nitrogen is the h_1 region. We use this as the initial configuration to study the oxygen adsorption. Our results are summarized in Table III. We find that oxygen bonds preferentially to free silicon dangling bonds. The lowest-energy configuration consists of the oxygen atom sitting on top of an unpassivated silicon. The oxygen adsorbs to a bridge site at a cost of 0.14 eV on this surface. This is in contrast to the isolated oxygen adsorbed on the clean surface.

The lowest-energy configuration consists of an nitrogen and oxygen atoms lying in distinct h_1 region, thus not sharing any silicon-surface bonds. In this location the nitrogen atom bonds to three silicon atoms while the oxygen bonds to

TABLE III. Energy differences for a single O atom to adsorb onto various sites of the $\frac{1}{9}$ ML coverage of N on the 4H-SiC (0001) surface. The lowest-energy (labeled Ot) corresponds to an oxygen atom adsorbing on top of an Si atom in an h_1 region which does not contain an N atom. The next highest energy (Ob) occurs when an O atom bonds to two unpassivated Si atoms. The higher-energy configurations consist of an NO molecule bonded to three Si atoms as described in the text or an NO molecule located above an Si atom with the N bonded to the Si (NOt) or the O bonded to the Si (ONt).

$\frac{1}{9}$ ML N+O	ΔE (eV)
Ot	0.00
Ob	0.14
NO	1.86
NOt	3.57
ONt	5.75

the top of a single silicon atom. We have calculated the binding of an NO molecule on the surface. The cost in energy to introduce an oxygen between a nitrogen-silicon bond is 1.16 eV compared with the nitrogen and oxygen atoms bonded in distinct h_1 regions. These findings are in approximate agreement to those of theoretical studies of NO on the Si(001) surface which find the atomic-adsorbed species to be more stable than the molecular species on the surface.[34,35] Furthermore, using the barrier analysis method described above, we find the oxygen and nitrogen strongly repel each other. Because of the mobility of the two atoms on the surface we were not able to form NO bonds using this method. Therefore we conclude that at low coverages of preadsorbed nitrogen, oxygen will preferentially bond to free silicon dangling bonds and not to nitrogen.

This does not exclude molecular NO from adsorbing onto the surface and we have considered a number of possible configurations. Other high-energy possibilities are for the NO molecule to attach to a silicon dangling bond via either the nitrogen or the oxygen. In these two cases the NO dangles from the surface. We find that the nitrogen attaches preferentially to the surface. This can be accounted for by considering that if the oxygen forms a single bond with the nitrogen and a single bond with the silicon surface, then the nitrogen has two dangling p orbitals. On the other hand, if the nitrogen forms a single bond with the surface and a double bond with the oxygen, there are no dangling bonds on the adsorbed NO.

The findings at $\frac{2}{9}$ ML coverage of nitrogen are consistent with the $\frac{1}{9}$ ML results. In our unit cell a single oxygen atom attaches to the unpassivated silicon dangling bonds in preference to bonding at the nitrogen-passivated h_1 regions. At this coverage, the cost in energy to drive an oxygen in between a nitrogen atom and one of the surface-silicon atoms is 1.64 eV as compared to the oxygen occupying a vacant silicon dangling bond. We find again at this coverage that the oxygen attaches on top of a single silicon dangling bond in preference to the bridge site between two silicon atoms.

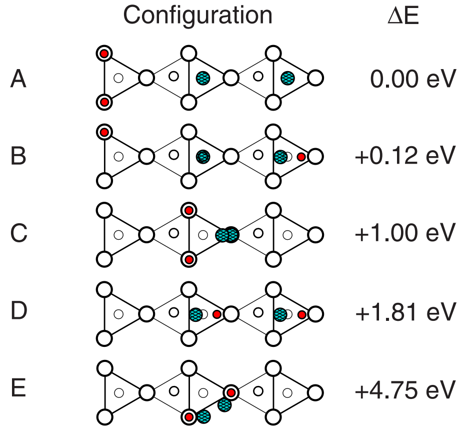

FIG. 2. (Color online) Schematics of the $\frac{2}{9}$ ML coverage consisting of equal parts nitrogen and oxygen. Each schematic may be considered a strip of h_1 regions running along the (110) direction in Fig. 1. The labeling is the same as in that figure. In addition, the small filled (red) circles represent oxygen atoms, the larger filled circles (blue) represent nitrogen atoms. Oxygen and nitrogen bonds have not been included. The thicker triangles are intended to emphasize the h_1 regions. The right-hand column lists the total energies in eV per surface slab relative to the lowest-energy configuration.

Figure 2 is a schematic showing the five lowest-energy configurations consisting of equal coverages of nitrogen and oxygen which correspond to $\frac{2}{9}$ ML coverage of both nitrogen and oxygen. In our 3×3 unit cell this corresponds to two oxygen atoms. The schematic is constructed similar to Fig. 1 except that we include only the necessary atoms to depict the $\frac{2}{9}$ nitrogen- and oxygen-covered surface in the vicinity of the relevant h_1 regions. For the lowest-energy configuration the nitrogen and oxygen do not form a bond [see Fig. 2(A)] so that they occupy different h_1 regions. The cost to insert the second oxygen between one of the nitrogen-silicon bonds drops to 0.23 eV as compared to the case of adsorbing a single oxygen onto the surface cell, and results in a configuration depicted in Fig. 2(B). The large reduction in energy for the oxygen insertion is likely due more to a decrease in the binding energy of the oxygen atom than an increase in the binding at the NO site. This can be understood by considering that at $\frac{2}{9}$ ML coverage of nitrogen, for every nine silicon-surface dangling bonds, six are passivated by adsorbed nitrogens located in two h_1 regions, leaving three dangling bonds unpassivated. The first oxygen adsorbs onto one of these dangling bonds. Because of the high electronegativity of the oxygen, there is a charge transfer from one of the remaining silicon-surface dangling bonds which fills the oxygen p shell, increasing the bond strength of this oxygen while leaving a single dangling bond available on the surface of the cell. This leaves the remaining oxygen only a single surface state to bond to. The transfer of the electron leaves the oxygen in an O^{2-} oxidation state while one of the surface-silicon atoms is left in an Si^{+} charged state. This effect is observable in the all coverages of oxygen where there are sufficient silicon-surface atoms to donate the dangling electron to the oxygen. This is consistent with experiments which find a Si^{+} oxidation state.[13,41]

The availability and transfer of dangling-bond electrons is likely to play a major role in the surface reactions and stabilization so it is worthwhile to consider this last issue in more

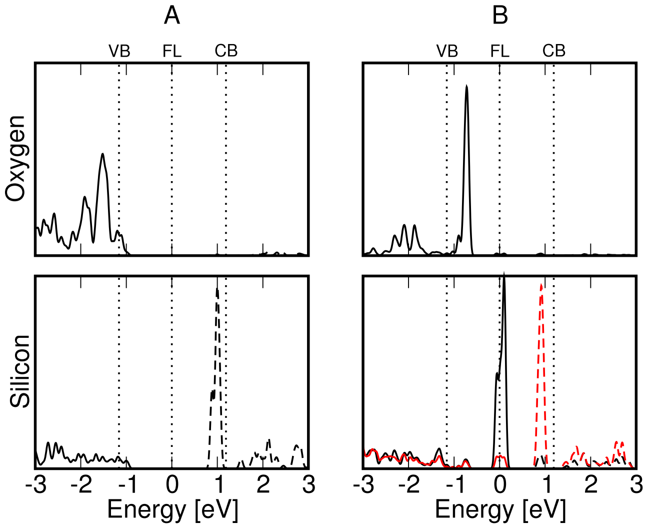

FIG. 3. (Color online) The PDOS for the oxygen atoms (top panels) and unpassivated silicon atoms (bottom panels) depicted in Figs. 2(A) and 2(B). Columns A and B correspond to the h_1 regions in Figs. 2(A) and 2(B), respectively. The thick curves plot the filled states and the hatched lines plot the empty states. The lower panel in column B plots the PDOS for the two unpassivated silicon atoms separately in black and gray (red). The vertical hatched lines represent the bulk-terminated 4*H*-SiC VB, FL, and CB, respectively. The bulk Fermi level was shifted to 0 eV while the slab curves were shifted so that the lowest-layer valence-band edge coincides with the bulk-terminated valence-band edge.

detail. In Fig. 3, we include the projected density of states (PDOS) for the oxygen-only adsorbed h_1 regions pictured in the schematic of Figs. 2(A) and 2(B). To aid in reading the graphs we have included vertical hatched lines to indicate the valence band (VB), Fermi level (FL), and conduction band (CB) for bulk-terminated 4*H* SiC. The bulk Fermi level has been shifted to 0 eV. The density of states were aligned as follows. The shift required to align the deepest SiC-layer valence-band edge of the surface cell with that of the bulk-terminated 4*H* SiC was determined and the layers shown in the PDOS were shifted by that amount.

This figure consists of two columns of two panels each. On the left (column A in the figure) are the PDOS for the case where the nitrogens are adsorbed in separate h_1 regions and the two oxygens are adsorbed in a common h_1 region. The top panel indicates that the two oxygen atoms do not contribute states in the bulk 4*H*-SiC band gap. The lower panel shows the empty state (hatched curve) corresponding to the vacant surface-silicon dangling-bond orbital, thus the silicon atom is missing an electron. The top panel on the right (column B), shows that the single oxygen exhibits one high-energy filled state lying just above the bulk valence-band edge. There are two surface-silicon atoms in this h_1 region. The PDOS for them are plotted separately in the lower panel (column B) in black and gray (red online). One of them has a filled state (solid curve) at the bulk Fermi level while the other has an empty state (hatched curve) in a similar position to that of the silicon atom in column A. These are in the same proximity as the silicon dangling-bond states for the clean 4*H*-SiC silicon surface. Furthermore, the high-energy peak corresponds to a silicon atom which is displaced downward, toward the surface by 0.3 Å from the average height of the silicon atoms on the surface. The other peak corresponds to the other silicon atom which is not displaced from the average height. A similar downward displacement occurs for the single unpassivated surface-silicon atom of Fig. 2(A).

We make one final observation. We have projected the net spin of each atomic site. We find that for the two oxygen atoms on an h_1 site, each oxygen has a net local moment of about $\hbar/4$ which is consistent with incomplete filling of the oxygen p shell. There are only three silicon dangling-bond electrons available for bonding whereas each oxygen must be supplied with two electrons to fill its valence shell. The unpassivated dangling-bond electron is donated with a moment of $\hbar/2$ distributed over two oxygen atoms. The surface silicon in this region has a negligible net moment since the electron has been transferred to the two oxygen atoms and it therefore has no unpaired electrons. For the oxygen in panel B, the net local moment is zero, consistent with the transfer of one electron to fill the oxygen p shell while one of the silicon atoms has no net moment and the second has a net moment of slightly less than $\hbar/2$. Please note that oxygen requires two additional electrons to fill the p shell, however for the silicon top-bonded oxygen, we implicitly assume this to contribute one of the two electrons.

The remaining three configurations depicted in Fig. 2 are at least 1.00 eV higher in energy per surface cell. They cannot be discounted purely on the unfavorable energetics. The NO and N_2 molecules do not dissociate on the surface easily. The barrier to forming an N_2 from two surface-bound nitrogen atoms is about 3.7 eV. The dissociation barrier for the surface-bound N_2 to break into two surface-bound nitrogen atoms is about 4.7 eV. Up to $\frac{1}{3}$ ML coverage of nitrogen, our barrier calculations indicate that surface-bound atomic nitrogen and atomic oxygen strongly repel both surface-bound nitrogen atoms and surface-bound oxygen atoms. Likewise NO molecules strongly repel each other once bound to the surface. For these reasons we believe that the end product strongly depends upon the composition of the adsorption species. As a result of the reduced availability of unpassivated silicon-surface states, the three high-energy configurations become the templates for surface structures at and above $\frac{1}{3}$ ML. The configurations of nitrogen and oxygen depicted in (C) and (E) of Fig. 2 become the lowest-energy arrangements at $\frac{2}{3}$ and 1 ML, respectively, while the configuration depicted in (D) is likely to represent a stable phase when the adsorption species is molecular NO.

Before proceeding to higher coverages of nitrogen and oxygen, we first consider the bond strengths of oxygen and nitrogen on the Si surface using Eq. (1) above. If the reference energy is taken from isolated nitrogen and oxygen atoms, respectively, we find that the bond strength of the O-Si bond is stronger than the three N-Si bonds combined. We find the bond strength of oxygen to the top of a silicon atom is 7.30 eV whereas the nitrogen-bond strength to three surface-silicon atoms is 6.73 or 2.24 eV/bond. For the oxygen bonding to a bridge site, the bond strength is 3.68 eV/bond. Thus, although oxygen should be able to displace nitrogen on the silicon surface when they are competing for

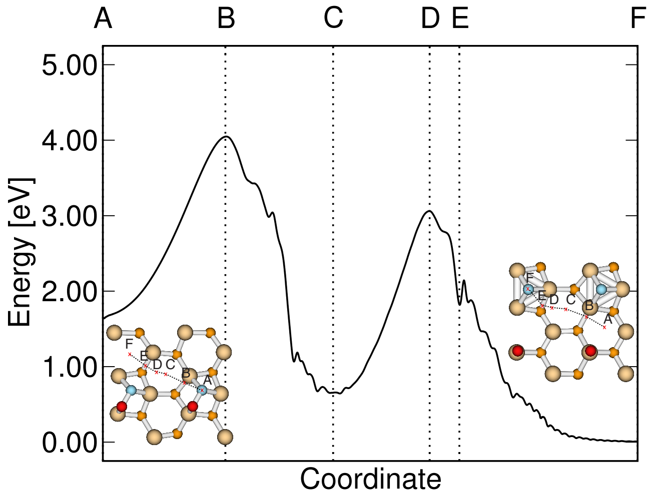

FIG. 4. (Color online) A plot of the total energy in eV for a nitrogen atom migrating along the 4*H*-SiC silicon-surface bilayer. The initial configuration is labeled A and pictured in the inset on the left of the graph. The final configuration is labeled F and pictured in the inset on the right of the graph. The atoms are identified as follows: (colors in parenthesis) nitrogen-dark gray circles (blue), oxygen-small light-gray circles (red), silicon-large light-gray circles (beige), and carbon-small medium gray circles (orange). Several points along the migration path are indicated by dotted vertical lines and indicated in the insets. The zero of energy is the lowest-energy configuration located at F. Point B is for the nitrogen located at the bridge site between two silicon atoms. Point C is for the nitrogen located in a neighboring h_1 region from the starting region. Point D is the top of the barrier between the h_1 region at C and the final h_1 region at F. Point E is in the h_2 site between the latter two h_1 sites. The surface used for the calculation contained a single NO molecule which corresponds to a coverage of $\frac{1}{6}$ ML of NO.

bonding sites, oxygen does not spontaneously migrate to nitrogen-bonded silicon.

Figure 4 is a plot resulting from a barrier calculation as described in Sec. II. In this calculation, the nitrogen was forced to increment along the surface given the starting coordinate at the point labeled “A” in the graph and the end point labeled “F.” The duration of the calculations was approximately 1.5 picoseconds. The inset figure on the left of the graph shows the starting configuration and the approximate trajectory of the nitrogen atom as it migrates across the surface. To capture the complete environment of the migrating atom, the figure shows approximately two unit cells of the $\frac{1}{6}$ ML NO-adsorbed surface used for the calculation. The inset on the right shows the final configuration at the point labeled F. The point labeled “B” coincides with the top of the barrier in which the nitrogen-oxygen bond breaks. This indicates an activation barrier of about 2.4 eV for an NO to dissociate into a nitrogen atom and an oxygen atom. At point “C” the nitrogen has migrated to a new h_1 position while the oxygen locates on top of a silicon atom where it stays for the remainder of the calculation. Point “D” is a bridge site separating an h_1 and an h_2 site (point “E”). In the final position the nitrogen sits in a low-energy h_1 site. Table IV summarizes the relative energies at each point identified on the graph. One interesting feature of this graph is the difference in energy between the nitrogen adsorbed at C and at F. The position C is higher in energy by 0.64 eV despite being a roughly similar environment to that of position F. One important difference not clearly visible in the graph is that the oxygen is not residing at its equilibrium position while the nitrogen is at C, thus the oxygen atoms may act to enhance the mobility of the nitrogen atoms. The difference in energy between the A and F configurations is 1.63 eV which is similar to the energy difference between a nitrogen and oxygen atom residing in different h_1 regions and an NO in one h_1 region at a coverage of $\frac{1}{9}$ ML NO.

TABLE IV. The relative energy for selected points along the potential-energy surface connecting an NO molecule adsorbed at position A (see inset on left) and the dissociated surface-adsorbed molecule at position F (see inset on right).

Position	ΔE (eV)
A	1.63
B	4.03
C	0.64
D	3.04
E	1.81
F	0.00

V. OXYGEN ADSORPTION ON THE NITROGEN-PASSIVATED SURFACE

A. $\frac{1}{3}$ ML NO

It has been established that at low coverages, oxygen does not bond preferentially to previously nitrogen-adsorbed sites. We now turn to the question of what happens as oxygen is adsorbed onto a $\frac{1}{3}$ ML nitrogen-passivated surface. Starting at $\frac{1}{9}$ ML of oxygen adsorbed onto this surface, we found that the lowest-energy configurations occur when oxygen and nitrogen are not bonded together and they do not bind to the same surface-silicon atoms. For the $\frac{1}{3}$ ML nitrogen-passivated surface discussed in Sec. III such constraints do not exist since the nitrogens occupy all the silicon dangling bonds. Two possibilities are indicated in Fig. 2. One low-energy configuration is for the oxygen to insert between one of the nitrogen-silicon bonds [see (B) in that figure for an example]. A second possibility is for the nitrogen to be displaced by the oxygen to form a surface-bonded N_2. In this case the N_2 dangles from a single silicon site in the h_1 region thereby adding two additional silicon-surface states as compared with the atomic nitrogen which bonds to three silicon-surface states. The additional states are available to bond with the oxygen.

At $\frac{2}{9}$ ML, an N_2 is bound to the surface by 0.52 eV relative to a gas-phase N_2 and a surface slab with $\frac{2}{9}$ ML oxygen. This is fairly weak binding compared to atomic oxygen or nitrogen or molecular NO (6.53 eV binding energy) on the surface. In fact, by $\frac{1}{3}$ ML for equivalent concentrations of oxygen and nitrogen on the surface, there are insufficient electrons to satisfy the shell filling of the oxygens. In the

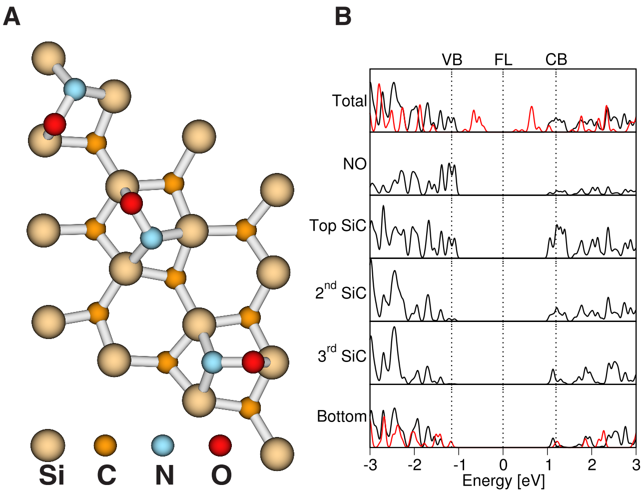

FIG. 5. (Color online) (a) A top view model of the $\frac{1}{3}$ ML coverage of NO on the 4*H*-SiC Si surface showing the NO and the surface SiC layer. The bonds are included to aid the eyes and do not necessarily represent actual chemical bonds. Atoms are labeled in the figure. All subsequent figure models use the same color scheme. (b) The layer-resolved density of states for the $\frac{1}{3}$ ML coverage of NO on the SiC Si surface including the total density of states (top graph) and the H-terminated bottom bilayer of the slab (bottom graph). The red lines represents the total density of states for the unpassivated (1×1) surface cell (top graph) and bulk total density of states (bottom graph). The black vertical hatched lines correspond, respectively, to the valence-band, Fermi-level, and conduction-band edges of the bulk SiC.

competition for surface dangling-bond electrons, the N_2 loses out and becomes unbound relative to gas-phase N_2. Another complication is that our barrier estimates for surface-bound nitrogen atoms to combine to form a surface-bound N_2 costs about 3.7 eV. The formation of such bonds only occurs for sufficiently high concentrations of nitrogen on the surface that nitrogen migration is not possible without involving nitrogen-nitrogen collisions otherwise the nitrogen atoms repel and displace each other. This is, however, not the last we have heard of the surface-bound N_2 as will be explained shortly.

Using the barrier method described in Sec. II we were not able to stabilize the oxygen in the nitrogen-passivated h_1 regions to form nitrogen-oxygen bonds for coverages up to $\frac{1}{3}$ ML. The oxygen and nitrogen repel each other. As an oxygen migrates into an h_1 region occupied by a nitrogen atom, the nitrogen migrates away from the oxygen. The process results in the nitrogen bonding to a surface-bilayer carbon atom and the oxygen bonding at a bridge site in the h_1 region. Therefore we conclude that the migration of oxygen on the nitrogen-passivated surface will not result in the formation of an NO surface at coverages up to $\frac{1}{3}$ ML of nitrogen. This work suggests that the nitrogen is continually displaced as more atomic oxygen is added. When the nitrogen is located in regions in which all of the surface-silicon sites are bonded to oxygen atoms we find that the nitrogen forms bonds with surface-bilayer carbon atoms as shown in Fig. 5. Given that the most stable configuration for nitrogen and oxygen to coexist on this surface is not easily accessible from the atomic constituents it is suggested that the source composition, i.e., atomic or molecular and molecular composition, plays an important role in the final surface adsorbate structure and composition.

For equal concentrations of nitrogen and oxygen at a coverage of $\frac{1}{3}$ ML, the lowest-energy stable configuration is formed by the adsorption of intact NO molecules. Analogous to the unoxidized, nitrogen-passivated surface, there are no silicon-surface states. The oxygen atom in the NO molecule forms a single bonds to one of the silicon atoms in an h_1 region and to the nitrogen atom while the nitrogen forms single bonds to the remaining two silicon atoms in the region. Thus if we assume a molecular NO source the following picture evolves. At low coverages of NO, the NO favors locating in h_1 regions on the surface. At $\frac{1}{3}$ ML, given time to equilibrate, all the h_1 sites are occupied and there is a regular array of NO adsorbed onto the surface. If there exists a mechanism to drive the NO molecules into the low-energy h_1 sites then this should result in a stable phase of NO on the surface. Our study indicates that barriers to migration on the surface for NO are rather large. The activation energy to go from a low-energy h_1 site to an adjacent h_1 that shares a silicon bond with a neighboring NO molecule is about 3.3 eV. To move back across the barrier to the low-energy site requires about 2.0 eV. This barrier height estimate neglects thermal effects which may facilitate the migration, given the energy difference between the two h_1 sites of about 1.3 eV.

At this coverage the NO molecules are arranged on the surface such that neighboring NO are rotated by 120° with respect to each other as in Fig. 5(A). This forms a (3×3) surface pattern which differs from the $(\sqrt{3}\times\sqrt{3})R30°$ formed by the nitrogen-only passivated surface. The oxygen atoms are raised above the nitrogen by 0.39 Å relative to the plane described by the silicon surface. The nitrogen-silicon bonds (1.90 Å), oxygen-silicon bonds (1.73 Å), and nitrogen-oxygen bonds (1.47 Å) are somewhat longer than would be expected from purely covalent single bonds (1.72, 1.61, and 1.45 Å, respectively). The disagreement is small however it is perhaps large enough to imply that there are effects in play such as surface strain. In fact, we find the silicon-silicon bond separation distances to be 2.68 Å (Si-Si distance for the Si-O-Si bond) and 2.9 Å (Si-Si distance for the Si-O-N-Si bond) for the surface with adsorbed NO, as compared with 3.1 Å for the clean silicon surface. Further evidence for this latter comes from the observation that the chemical potential continuously decreases with increasing coverage up to $\frac{1}{3}$ ML as will be discussed in Sec. VI.

Figure 5(B) shows the PDOS for the surface adsorbed with $\frac{1}{3}$ ML of NO. The three surface states lying at the bulk valence-band edge, from -1.4 to -1.1 eV are π^*_{2p} antibonding states originating with the NO molecule. The PDOS also shows that upon oxidation, states appears in the gap just below the conduction-band edge. They are associated with the surface-layer silicon atoms. It is not clear whether these states lie below the conduction-band edge since the Fermi level was used to align the slab DOS with that of the bulk (gray line on bottom graph). Because the slab is of finite thickness the surface states are heavily weighted which could artificially shift the Fermi level down in energy. If we were

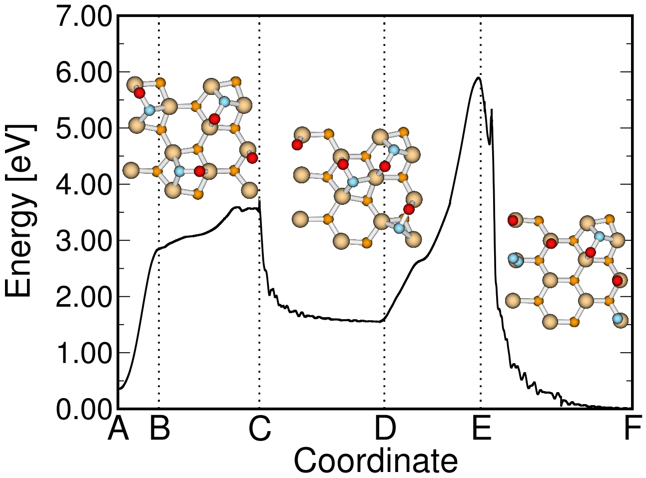

FIG. 6. (Color online) A plot of the total energy in eV for a nitrogen atom migrating along the 4*H*-SiC silicon surface. The surface used for the calculation is the $\frac{1}{3}$ ML NO surface. The relevant region of the initial configuration is labeled A and pictured in the inset to the right of the *y* axis. The relevant region of the final configuration is labeled F and pictured in the inset on the right. The intermediate stable configuration at D is pictured in the inset located in the center of the graph. The color scheme used is the same as that in Figs. 4 and 5(A). The zero of energy is the lowest-energy configuration located at F. Point B is for the nitrogen located at the bridge site between two silicon atoms. Several points along the migration path are indicated by dotted vertical lines. From B to C the NO molecule migrates over a silicon atom with the nitrogen dangling from the oxygen. The point E is the top of the barrier separating the NO at the h_1 site indicated by D and the h_2 site between D and F. To the right of E, the saddle point corresponds to the NO moving through the h_2 region.

to, instead, align the bulk valence-band edges from the bulk configuration and the NO-adsorbed configuration these states would be moved above the bulk conduction-band edge. For comparison we have included the DOS of the clean unreconstructed surface from a spin-polarized DFT calculation which shows the Mott-Hubbard bands as found in recent experiments.[42] We leave the exact alignment of the band edges as an open question for more accurate methods.

As was done for the lower coverage we introduce a plot of the energy barriers in Fig. 6. Also included is a table (see Table V) summarizing the energy at various points along the path. In this case the oxygen is dragged across the surface. Position A corresponds to the $\frac{1}{3}$ ML of molecular NO on the surface as shown in the inset. Between positions B and C the NO is migrating over an h_2 site which has a carbon atom in the surface bilayer. The NO is dangling from the top of a silicon atom bound to the surface via the nitrogen atom. Position D corresponds to a high-energy h_1 site in which the NO shares silicon-surface bonds. Note that in driving the NO into this site, the NO in the upper left of the inset for position A has been moved out of the field of view, thus illustrating the mutually repulsive nature of the adsorbed NO. The top of the barrier at E corresponds the NO locating at a bridge site. Just to the right of E corresponds to the NO sitting in an h_2 site showing the local minimum with a barrier of about 0.2 eV. The final position at F corresponds to the formation of an N_2 molecule and two oxygen atoms, each sitting on top of a single silicon atom. The barrier between D and E suggests a barrier of about 4.3 eV to the formation of an N_2 from two NO molecules at this coverage which is somewhat higher than the barrier for two nitrogens to form an N_2 of about 3.7 eV.

TABLE V. The relative energy for selected points along the potential-energy surface connecting an NO molecule adsorbed at position A (see inset on left) and the dissociated surface-adsorbed molecule at position F (see inset on right).

Position	ΔE (eV)
A	0.34
B	2.84
C	3.53
D	1.54
E	5.86
F	0.00

B. One additional oxygen

In Sec. V B and the next we are interested in determining what happens as additional oxygen is added to the surface at a fixed $\frac{1}{3}$ nitrogen coverage. We begin with the lowest-energy stable 3×3 surface with $\frac{1}{3}$ ML NO configuration discussed in the previous section. The oxygen atom is added to various locations in the vicinity of a single h_1 region and between two h_1 regions. Multiple configurations are optimized to determine the lowest-energy configuration. We pay particular attention to two issues which have arisen during the introduction of nitrogen onto the SiC Si face. The first is the depletion of nitrogen from the silicon face and the second is the formation of nitrogen-carbon bonds.[17,43] We are able to identify a path for the dissociation of an NO molecule upon oxidation of the face. We also find that for a sufficient oxygen concentration at the surface, nitrogen-carbon bonds form. It is stressed at the outset of these two sections that our studies do not include temperature effects and are thus only suggestive of surface effects due to oxidation.

For the lowest-energy configuration consisting of adsorbed NO molecules, upon the adsorption of a single additional oxygen atom the NO molecule migrates to an h_2 region as shown in Fig. 7. The h_2 region is similar to the h_1 region except that a carbon atom is present in the top bilayer centered between the three surface-silicon atoms. The adsorbed oxygen atom bonds to the top of a single silicon atom in the h_1 region. For this surface we find a small shift in the oxygen chemical potential relative to the $\frac{1}{3}$ ML NO-adsorbed surface from $\mu = -2.47$ to -2.23 eV relative to an oxygen adsorbed on the clean 4*H*-SiC silicon surface.

The carbon atom is displaced from its original position downward toward the next lower bilayer and to one of the nitrogen-bonded silicon atoms. The downward displacement is small and amounts to about 0.05 Å or 3% of the Si-C interlayer spacing. The bond lengths to the three nearest-neighbor silicon atoms within the surface bilayer are 1.80,

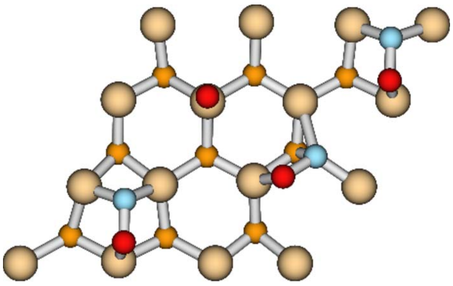

FIG. 7. (Color online) The SiC surface bilayer with $\frac{1}{3}$ ML adsorbed nitrogen and 4/9 ML O. See Fig. 5(A) for a description of the atom types.

1.85, and 2.68 Å and the distance to the nitrogen atom is 1.56 Å. The typical bond lengths for the surface-bilayer carbon-silicon bonds on the nitrogen-adsorbed surface range from about 1.85 to 1.95 Å for the silicon-centered carbon atoms so this is an indicator that there is some nitrogen-carbon bonding taking place. An analysis of the charge density and the wave functions indicate that there is σ bonding between the nitrogen and carbon in the surface bilayer.

C. Two additional oxygens

TABLE VI. The nitrogen-oxygen bond lengths, respectively, for a displaced NO adsorbed onto the surface shown in Fig. 8, an NO adsorbed on top of the reference surface with $\frac{1}{9}$ ML NO coverage, and three charge states of the isolated gas-phase NO molecule. In the second column are the N-Si bond lengths for the respective surfaces.

Structure	N-O bond length (Å)	N-Si bond length (Å)
Displaced NO	1.16	2.21
$\frac{1}{9}$ ML NO (top)	1.24	1.85
NO^-	1.22	
NO^0	1.16	
NO^+	1.08	

For the adsorption of a second oxygen onto the 3 × 3 NO-adsorbed surface the lowest-energy configuration, pictured in Fig. 8, is the result of adding oxygen to the highest-energy configuration from the single oxygen adsorption study. There are two notable changes to this surface which are circled in (B) and (C) of that figure. The first change is that the NO molecule which was located in the h_2 region has been displaced away from the surface and is tethered by a long bond to an Si surface atom [see Fig. 8(B) and inset]. In fact, at this coverage the two lowest-energy surfaces explored in this study are characterized by a similar displacement of an NO molecule away from the surface. Because of the unusually long bond length this presents one possible dissociation path for the nitrogen. By examining the bonding of this NO it may be possible to gain some insight into the nitrogen depletion observed at the surface upon reoxidation as noted in.[23,24]

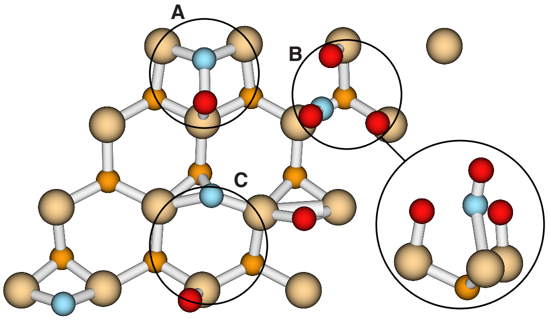

FIG. 8. (Color online) A top view of the passivated SiC surface bilayer $\frac{5}{9}$ ML coverage of O showing the three distinct features formed at this coverage. (a) is the NO molecule found at lower coverages of oxygen. (b) A NO molecule which is dissociating from the surface including an inset showing a side view of this h_1 region. (c) A nitrogen which has inserted between an Si and a C in the surface bilayer. Due to periodic boundary conditions, the leftmost atoms are equivalent to the rightmost and top atoms equivalent to the atoms at the bottom.

In Table VI for the lowest-energy configurations we compare the N-O bond lengths for the NO on the surface, in the region of high oxygen concentration to that of various charge states of the NO molecule. We also include the bond lengths for a $\frac{1}{9}$ ML coverage NO located on top of an Si atom, with the N bonded to the Si as a reference. From this table we observe that the NO exhibits a Si-N bond to the surface which is 20% longer than that of the $\frac{1}{9}$ ML reference surface bond. For the reference NO, the N-O bond length is similar to that of an anionic NO molecule while that of the displaced NO is similar to that of a neutral NO. We propose that the depletion of N from the surface takes the form of an oxygen coming into the surface and an NO leaving. We consider three possible paths

$$NO_{ads} \rightarrow NO^- + \mathrm{surf}^+ + 1.21 \ \mathrm{eV},$$

$$NO_{ads} \rightarrow NO^0 + \mathrm{surf}^0 - 1.97 \ \mathrm{eV},$$

$$NO_{ads} \rightarrow NO^+ + \mathrm{surf}^- - 12.26 \ \mathrm{eV}, \qquad (3)$$

where NO_{ads} indicates the slab surface including the adsorbed NO molecule and surf^q are several of the possible charge states that the surface may be left in after the reaction. The path which releases an NO^- and leaves the surface with a positive charge state is the only exothermic pathway and will thus progress forward. We propose that the NO, once fully dissociated, leaves the surface with a net negative charge, in agreement with experiments which find a Si^+ oxidation state.[13,41] However, based upon the observed NO bond length in our model it is a neutral species at this point in the surface dissociation process.

A second rearrangement on the surface is that the nitrogen and oxygen of one NO molecule dissociate from each other. The nitrogen migrates to an h_2 region between two surface-silicon atoms while the oxygen migrates to the top of a silicon atom [see Fig. 8(C)]. As in Sec. V B charge-density and wave-function analyses indicate σ bonding between the nitrogen and the carbon atom below it.

This work seems to suggest that the nitrogen disrupts the surface-bilayer silicon-carbon bonds however this is a high-energy configuration relative to the formation of a nitrogen-oxygen bond. The nitrogen-carbon bond forms when oxygen migrates into an h_1 region which is occupied by a nitrogen atom. Our calculations indicate that upon addition of a third oxygen to this region there is no place for the nitrogen to bond on the surface. It is carried away in the form of NO^- gas. Once the NO has dissociated from the 3×3 surface, the surface coverage of the unit cell consists of three distinct h_1 regions, one of which is populated by an NO molecule, one which is populated by two oxygen atoms and one which is unpopulated. One nitrogen atom has migrated to an h_2 region. We found in Sec. IV that the oxygen is likely to be transient as the nitrogen and oxygen migrate to lower-energy surface sites.

VI. THE ADSORPTION SURFACE ABOVE $\frac{1}{3}$ ML N COVERAGE

A. The fundamental surface feature up to 1 ML

To investigate the oxidation effects as the coverage of nitrogen goes above $\frac{1}{3}$ ML we begin with the $\frac{1}{3}$ ML NO-adsorbed surface in a 3×3 cell as described at the beginning of the previous section. To that surface we add an additional nitrogen to one of the h_1 regions. This corresponds to a coverage of $\frac{4}{9}$ ML of nitrogen. For the additional nitrogen we add up to three oxygen atoms and examine multiple configurations for each subsequent oxygen atom. After sampling a number of configurations we find the lowest-energy surface described by Fig. 9(A). The lowest-energy configuration corresponds to a nitrogen disrupting an NO bond and combining with the previously adsorbed nitrogen. The resulting N_2 bond length is 1.13 Å which is just slightly longer than that of the gas-phase N_2. The structure was optimized starting with the nitrogen-nitrogen separation of 1.34 Å which is short enough to avoid barriers which would inhibit the formation of the nitrogen-nitrogen bonds. For this configuration we find that the N_2 is bound to the SiC surface by 0.09 eV relative to the ground state of the gas-phase N_2. This leaves the surface with a single silicon atom which is unpassivated in the unit cell. If a subsequent oxygen atom is added to that site, the coverage is equivalent to $\frac{4}{9}$ ML of NO shown in Fig. 9(B) however there are insufficient electrons to optimize the bonding of oxygen to the surface. Once again we find a competition between the N_2 and the atomic oxygen for silicon electrons and the nitrogen loses out. The N_2 is unbound with respect to gas-phase N_2 at this coverage.

An alternative arrangement results in the formation of an N_2O_2 molecule bound to the surface as shown in Fig. 9(B). The nitrogen-nitrogen bond length increases to 1.24 Å as shown in Table VII. Up to $\frac{1}{3}$ ML, a single NO molecule passivates three silicon dangling bonds in an h_1 region. Such a configuration results in a surface which lies about 1.9 eV higher in energy than the previously discussed configuration. We find that the addition of a second NO molecule to one h_1 region in this configuration results in only two surface dangling bonds being passivated, thus introducing a half-filled silicon-surface band into the band gap. Furthermore, it involves an N_2 bound to two oxygen atoms. This can convert to the lower-energy configuration by crossing an activation energy barrier of 0.2 eV. We have also considered configurations such as a N_3O_3 ring structure which is about 0.89 eV/NO higher in energy than the N_2O_2. Although the N_2O_2 configuration is high energy, it reappears at higher coverages as the most stable adsorption configuration. It is worthwhile considering that neither of the N_2 molecules in Figs. 9(B) and 9(C) are bound with respect to gas-phase N_2 (at zero

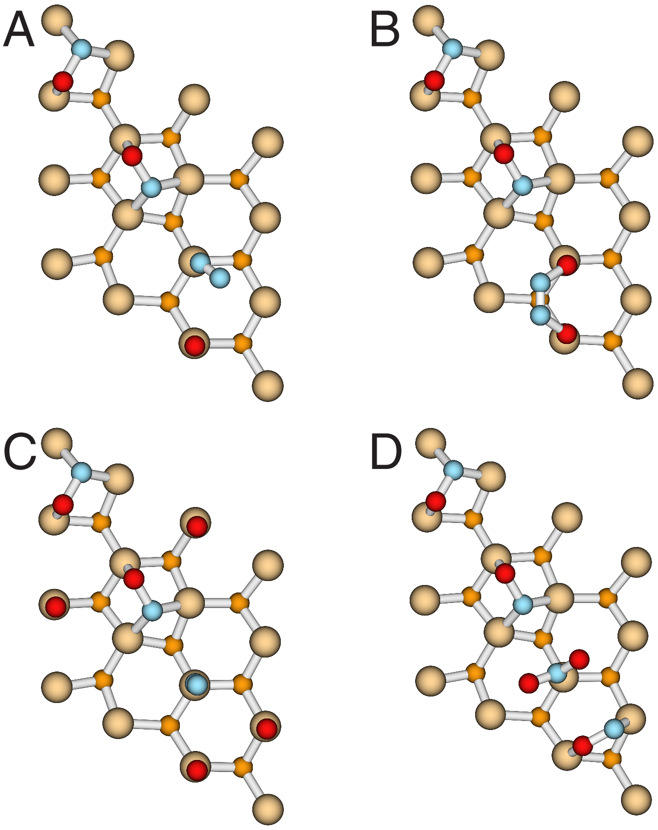

FIG. 9. (Color online) A top view of the $\frac{4}{9}$ ML coverage of nitrogen on the surface SiC bilayer with (a) $\frac{1}{3}$ ML of oxygen, (b) and (c) $\frac{4}{9}$ ML coverage of oxygen, and (d) $\frac{5}{9}$ ML of Oxygen.

TABLE VII. Bond lengths between Si, N, and O on the silicon surface. The first column data is for an oxygen inserted between the surface and adsorbed nitrogen. The second column is for an oxygen bonding to the top of the adsorbed nitrogen. The third column lists the DFT determined covalent bond lengths. The parenthesis indicate the bond order.

	Bond length Å		
	Si-O-N	Si-N-O	covalent
Si-N		1.85	1.72(1),1.56(2)
Si-O	1.70		1.61(1),1.48(2)
N-O	1.42	1.24	1.45(1),1.21(2)
N-N	1.24	1.48	1.42(1),1.25(2),1.11(3)

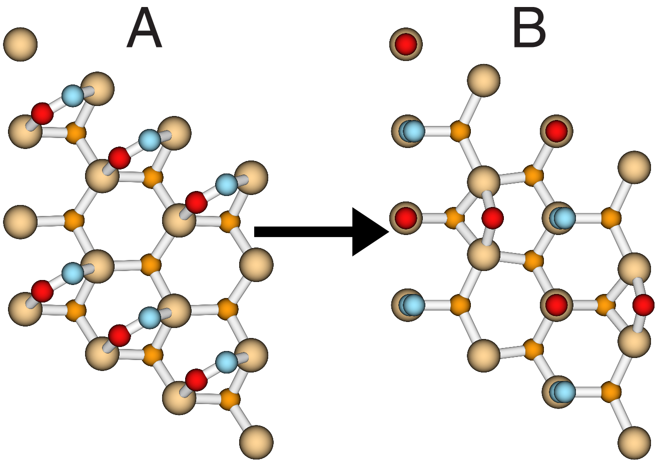

FIG. 10. (Color online) The (a) initial and (b) final configurations for the $\frac{1}{2}$ ML calculation. The atoms are labeled the same as those in Fig. 5(A).

temperature and pressure), the former is bound with respect to gas-phase NO while such a comparison is not relevant for the latter.

If we continue to add an additional adsorbed oxygen atom on the N_2O_2 surface it bonds to the exposed silicon dangling bond which resulted from the formation of the N_2O_2 configuration. Note that there are no surface sites for the oxygen to bond to on the lowest-energy $\frac{4}{9}$ ML NO surface. In this case the oxygen has a much stronger bond to the surface than N_2 and the N_2 can easily be displaced. Another alternative is for the N_2O_2 to split into an NO bonded to two silicon atoms and the second NO to bond to one, with the additional oxygen bonding to the nitrogen, forming a silicon-bonded NO_2 as shown in Fig. 9(D). The NO_2 is bonded to the surface by a nitrogen. Note that the NO has a nitrogen dangling bond and should be unstable. This lies 1.87 eV higher in energy than the configuration with an N_2O_2. The NO_2 is bound to the surface by 1.09 eV. Other configurations we considered led to dissociation of NO.

Finally in this section we consider the surface at $\frac{1}{2}$ ML of NO. We have considered only the case of adsorption of molecular NO onto the $\frac{1}{3}$ ML surface. We suppose building blocks as indicated in Fig. 9(D), namely, that each of the nitrogens in the surface-bonded NO molecules lose one of their surface bonds and an additional NO molecule is able to insert for every two such surface-bound NO molecules. In such a case the NO can be either aligned or antialigned. Figure 10 shows the initial configuration in (A) and the final configuration in (B). We see that the configuration is not stable for the parallel-aligned NO molecules. It transforms to the low-energy configuration consisting of a dangling N_2 bonded on top of one surface silicon and the oxygens bonded on top of the remaining two silicon atoms in an h_1 region. Although the $\frac{1}{2}$ ML coverage seems to exclude the formation of N_2O_2 on the surface at and above this coverage, this is not necessarily the case. Our model assumes a uniform growth of the configuration depicted in Fig. 10(A) whereas the surface is likely to be composed of a variety of the different adsorbates considered in this paper.

B. Covalent bonding of the adsorbate

Before continuing to higher coverages of nitrogen and oxygen we consider the bonding mechanism that governs the surface growth. Disregarding the configurations which include dangling N_2, the fully oxidized surface at $\frac{1}{3}$ ML of nitrogen is similar to that of the unoxidized surface in that each NO bonds to three surface-silicon atoms just as each nitrogen atom does. In the previous section we identified an oxidized configuration for coverages above $\frac{1}{3}$ ML of nitrogen which is also analogous to that of a nitrogen-covered surface, namely, the N_2O_2 surface is similar to the N_2 surface in that both bond to only two surface-silicon atoms. We have found that for coverages of nitrogen up to $\frac{1}{3}$ ML, the configuration for an NO molecule to bond to the top of a silicon atom is with the nitrogen bonding to the silicon and the oxygen bonding to the nitrogen. However above a coverage of $\frac{1}{3}$ ML nitrogen, the oxygens are inserted between the nitrogen atoms and the silicon-surface atoms. In other words, up to and including the $\frac{1}{3}$ ML coverage of nitrogen, the order in which the oxygens bond to nitrogens is reversed from that of the bonding above $\frac{1}{3}$ ML. This is related to the fact that up to $\frac{1}{3}$ ML, nitrogen atoms are able to exist on the surface without bonding to other nitrogen atoms while above this, the additional nitrogens form nitrogen-nitrogen bonds.

The difference between these two cases is easily understood in terms of simple chemical bonds. Below $\frac{1}{3}$ ML, when a nitrogen adsorbs onto the top of a silicon atom it forms a single bond. This leaves two *p* electrons available for forming a double bond with the oxygen and no residual dangling bonds. Switching the order of oxygen and nitrogen leaves the oxygen forming a single bond with the silicon, a single bond with the nitrogen and two unbonded *p* electrons from the nitrogen. Above $\frac{1}{3}$ ML the situation is that the nitrogens in the N_2 form a double bond with each other and a single bond with the silicon surface. If the oxygen is inserted between the nitrogen and silicon it forms a single bond with the silicon and a single bond with the nitrogen, leaving the nitrogen-nitrogen double bond in tact. These bond lengths are all very similar to the covalent bond lengths as can bee seen in Table VII. If the oxygen atoms bond on top of the nitrogens then within a covalent-bonding scheme the nitrogens form a single bond with the surface, a single bond with each other and a single bond with the oxygen atoms. This leaves the oxygen atoms each with a half-filled dangling bond. We find an extended bond between the silicon and nitrogen. This is weaker than a single bond in a covalent-bonding scheme while the nitrogen-oxygen bond is somewhere between a single and double bond in this scheme. The nitrogens are separated by 1.48 Å which is somewhat longer than the covalent bond length for a nitrogen-nitrogen single bond.

C. $\frac{2}{3}$ ML coverage and above

The surface growth pattern that evolves from what we have considered so far is as follows. Once adsorbed onto the silicon surface of 4*H* SiC, atomic oxygen, and atomic nitrogen repel each other and other atoms of the same species. As the density of oxygen and nitrogen increases on the surface,

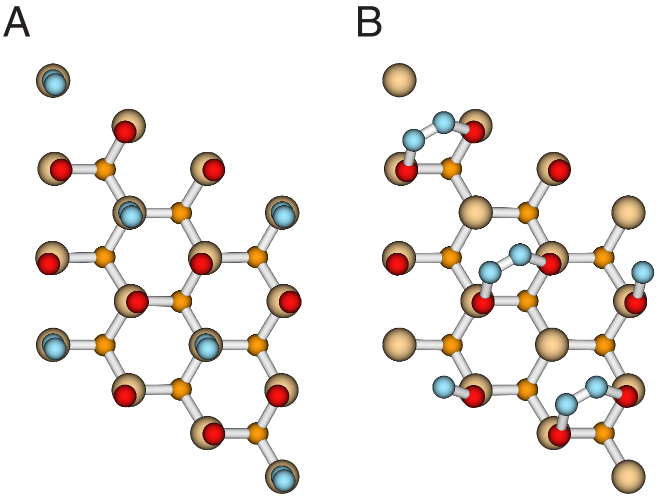

FIG. 11. (Color online) (a) The lowest-energy adsorption structure and (b) the next lowest structure at $\frac{2}{3}$ ML coverage of NO showing the surface SiC bilayer.

nitrogen is displaced. When it can no longer be displaced it either bonds with oxygen to form surface NO molecules or N_2 molecules. This situation becomes imminent at a coverage of about $\frac{1}{3}$ ML. As oxygen is further added to the surface, the nitrogen is carried away in the form of NO^- or more probably N_2 gas as illustrated in the discussion of the $\frac{1}{2}$ ML coverage in Sec. VI A. Thus, eventually, with sufficient oxygen, the nitrogen may be completely removed from the surface. The saturation coverage at which N_2 must be removed from the surface occurs at $\frac{2}{3}$ ML considering a growth path following the low-energy path, namely, h_1 regions adsorbed with two oxygen atoms and an N_2, each on top of a single silicon atom. We show this along with the higher-energy surface consisting of N_2O_2 molecules in Figs. 11(A) and 11(B), respectively. This latter lies about 2.27 eV higher in energy than the low-energy configuration.

The spin-polarized PDOS for these two configurations is shown in Figs. 12(A) and 12(B). In these graphs the top panel shows the total density of states for the $\frac{2}{3}$ ML NO-adsorbed surface in black. For comparison, in the top panels we have also included the total DOS for the clean 4*H*-SiC silicon-surface slab in gray (red online). This shows the Mott-Hubbard bands of the unreconstructed surface as found in recent experiments.[42] These states are predominantly present only in the surface SiC layer and are clearly the silicon-surface dangling bonds. To aid in referencing the states, the bulk valence band, Fermi level, and conduction band are indicated by hatched vertical lines. Also included is the bulk 4*H*-SiC total density of states (gray or red online) superimposed on the lowest panel of each graph, which shows the DOS for the lowest layer of the slab (black). The bulk Fermi level has been shifted to 0 eV and the lowest layer of the surface slab has been shifted so that the valence-band edge coincides with that of the bulk. All other layers have been shifted by this same amount. In all panels the

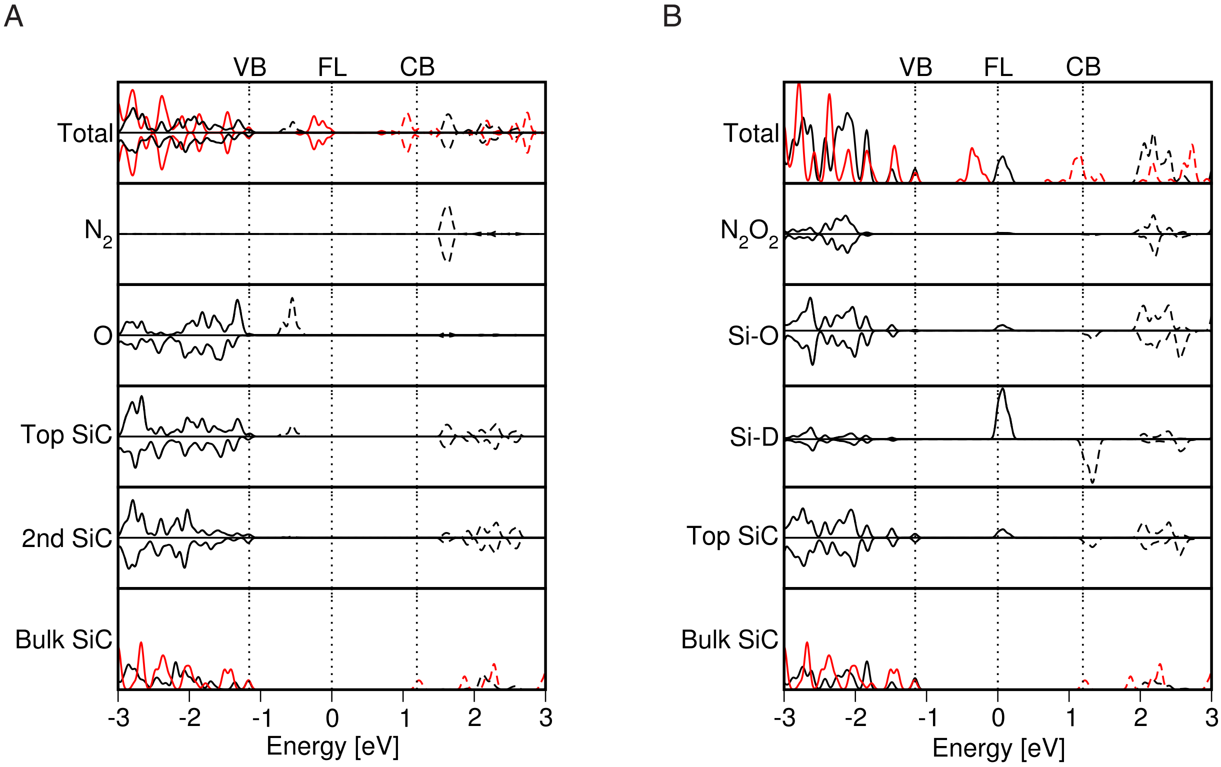

FIG. 12. (Color online) (a) The PDOS for the lowest-energy configuration at $\frac{2}{3}$ ML coverage of NO and (b) the higher-energy configuration presented in Fig. 11. The red hatched line on the graphs is the total DOS for the 1 × 1 surface cell (top graphs) and bulk (bottom graphs). The vertical hatched lines represent the valence-band and conduction-band edges, respectively, of the bulk SiC. The bulk Fermi level has been shifted to 0 eV. The lowest-layer valence-band edge of the surface slab has been shifted to align with that of the bulk-terminated valence-band edge and subsequent layers have been shifted by the same amount.

filled states are indicated by solid curves while the empty states are indicated by hatched curves. In Fig. 12(A) we see that the N_2 does not contribute states to the bulk band gap while there is an empty state due to the oxygen which pins the Fermi level of the surface slab about 0.5 eV above the valence-band edge. We note that the oxygen panel and the two subsequent panels project both spins, with the spin-minority densities printed as negative values. Although it cannot be seen directly from the DOS, the oxygen atoms each carry a local magnetic moment of about $\frac{\hbar}{2}\mu_B$ due to the lack of electrons to complete their p orbitals.

Assuming a high-energy growth process which allows the formation of the N_2O_2 molecules, the molecules populate more of the h_1 sites until at $\frac{2}{3}$ ML, $\frac{2}{3}$ of the silicon atoms are passivated and $\frac{1}{3}$ are unpassivated. This surface is depicted in Fig. 11(B). The spin-polarized layer-resolved DOS for this coverage is plotted in Fig. 12(B). The N_2O_2 molecules do not contribute states into the bulk band gap. Shown in separate panels are the two types of silicon atoms found on this surface, namely, those that are bonded to oxygen (Si-O) and those that are dangling. The empty and filled dangling-bond states are clearly visible and are shifted about 0.3 eV higher in energy than those of the clean surface. As with the oxygen atoms in the lower-energy configuration, these silicon atoms exhibit a local magnetic moment of about $\frac{\hbar}{2}\mu_B$. The exposed silicon-surface states represent an unfavorable configuration and as has been noted, the N_2 may migrate over a 0.2 eV activation barrier to form the low-energy configuration depicted in Fig. 11(A). Alternatively we find that the N_2O_2 can walk along the surface toward each other provided they can get across a 1.8 eV activation barrier. The resulting configuration packs the N_2O_2 molecules on adjacent silicon-surface sites covering $\frac{2}{3}$ of the surface while the remaining $\frac{1}{3}$ of the surface is unpassivated. This lowers the surface energy by 0.04 eV for a three silicon atom surface cell or 0.015 eV/1×1 surface cell. In addition, this stabilizes the N_2 on top of the oxygen atoms since there are no surface-silicon sites for them to bond to except at the boundary between the passivated regions and unpassivated regions.

The lowest-energy surface growth line, composed of surface-bound dangling N_2 and oxygen atoms comes to a halt at $\frac{2}{3}$ ML of NO since their are no more silicon-surface dangling-bond sites available. The higher-energy growth process continues up to 1 ML when all dangling bonds are again passivated as depicted in Fig. 13(A). At this coverage there are no longer any states in the gap as can be seen in Fig. 13(B). We also find that the valence-band edge is void of surface states. If the high-energy growth path continues from the onset at $\frac{1}{3}$ ML of NO up to the saturation of N_2O_2 on the surface at 1 ML, it could be observed that, as the coverage of NO goes from $\frac{1}{3}$ to $\frac{2}{3}$ ML, the density of states above the SiC valence-band bulk edge increases. Above that coverage it decreases steadily until it disappears all together at 1 ML.

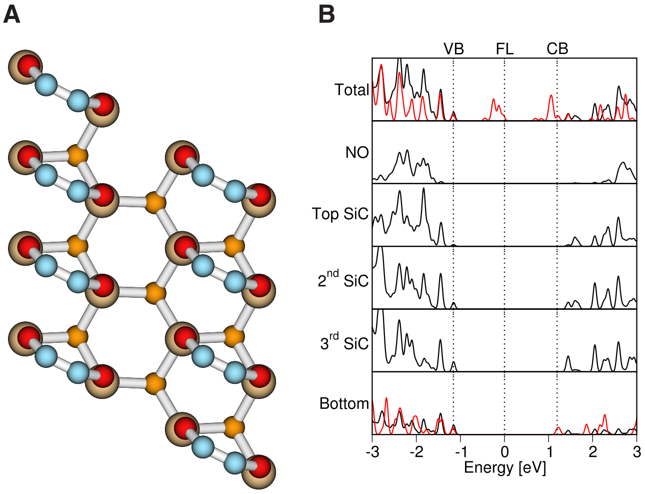

FIG. 13. (Color online) (a) The lowest-energy adsorption structure at 1 ML and (b) the PDOS for that configuration. The atoms in (a) are defined by the scheme presented in Fig. 5(A). The red hatched line on graph (b) is the total DOS for the 1×1 surface cell (top graph), and bulk (bottom graph). The vertical hatched lines represent the valence-band and conduction-band edges, respectively, of the bulk SiC. The bulk Fermi level has been shifted to 0 eV. The lowest-layer valence-band edge of the surface slab has been shifted to align with that of the bulk-terminated valence-band edge and subsequent layers have been shifted by the same amount.

Such a high-energy growth path may not occur for another reason which we explain with the following. Figure 14 plots the adsorption energy of NO per 1×1 unit cell. The slope of the solid line which indicates the low-energy envelope is the chemical potential at the given coverage.[40] The adsorption structures which lie above the tie line are only metastable and will decompose into combinations of structures which lie on the tie line. Therefore we find no structures between $\frac{1}{3}$ and 1 ML which are stable. We find that the chemical potential continually increases up to $\frac{1}{3}$ ML. It remains constant up to 1 ML. Above 1 ML of NO there is an increase in the chemical potential and there are no more surface bonding sites. These observations indicate that one stable phase occurs at $\frac{1}{3}$ ML and a second stable phase occurs at 1 ML. Coverages between $\frac{1}{3}$ and 1 ML will migrate until there are no surface dangling bonds available, forming patches on the surface composed of these two phases. Note

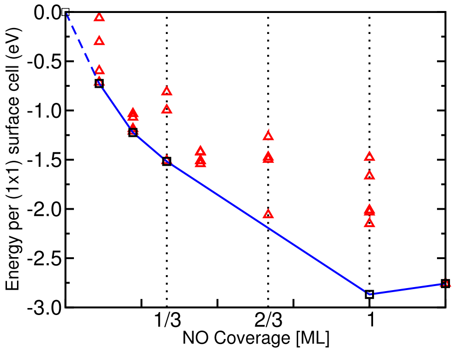

FIG. 14. (Color online) Plot of the adsorption energy of NO as a function of coverage per (1×1) unit cell. The □ indicate the lowest-energy structures examined at a given coverage. The △ indicate high-energy structures. The tie line, drawn to aid the eyes, indicates the low-energy boundary. Adsorption structures which lie on this line are stable, structures which lie above this line are metastable. Configurations containing dangling N_2 were excluded from this graph.

that the situation is complicated by the formation of N_2 when the NO coverage goes above $\frac{1}{3}$ ML. As we have mentioned earlier the N_2 are not bound with respect to gas-phase N_2 (at zero temperature and pressure). On the other hand they are bound with respect to gas-phase NO. It is possible that N_2 bound to surface oxygen is more stable than the N_2 dangling from a surface silicon due to a weakening of the nitrogen-nitrogen bond and a strengthening of the nitrogen-surface (oxygen vs silicon) bond. The graph excludes all configurations containing dangling N_2 in order to highlight the adsorbed NO configurations. The N_2 configurations would represent the lower bound envelope to the graph from $\frac{2}{9}$ to $\frac{2}{3}$ ML if they had been included.

VII. SUMMARY

In this work we have tried to draw a picture of adsorption and interaction of nitrogen and oxygen on the 4*H*-SiC surface. We have considered this from the standpoint of adsorption of atomic and molecular species. The lowest-energy configurations for coverages of between $\frac{1}{9}$ and $\frac{5}{4}$ ML have been identified and several barriers to surface reactions have been determined. We have also examined the effects of adsorption of surface states due to the silicon surface and the adsorbed species. Our general findings are that, once adsorbed onto the surface, atomic oxygen and nitrogen repel each other and are thus immiscible for some thermodynamic conditions. Once bound, though, NO forms a stable configuration on the surface. Oxygen bonds preferentially to the surface compared with nitrogen and the adsorbed oxygen will displace adsorbed nitrogen.

Up to $\frac{2}{3}$ ML coverage of nitrogen and oxygen the lowest-energy surface growth is for atomic oxygen to bond to the top of surface-silicon dangling bonds. Each oxygen requires two silicon-surface states for the lowest-energy bonding configuration. For this reason, although all silicon-surface states are passivated with either N_2 or atomic oxygen the bulk band gap is not state free. Each oxygen is missing an electron to fill it's *p*-electron shell and the resulting empty state appears just above the bulk valence-band edge. When the oxygen is sparse enough on the surface to permit it, nitrogen bonds at sites between three surface-silicon atoms. If the density of oxygen and nitrogen become sufficiently high the nitrogen atoms may combine to form N_2 molecules which dangle from the tops of surface-silicon atoms, thus increasing the number of surface-silicon states available. If the coverage of oxygen goes above $\frac{2}{3}$ ML, the N_2 dimers are displaced from the surface thus this is an upper bound to the adsorption of NO molecules onto the surface for the lowest-energy surface configuration. By 1 ML coverage of oxygen there are no N_2 dimers bound to the surface.

Up to $\frac{1}{3}$ ML of NO, a higher-energy configuration results from NO molecules bonding between three surface-silicon atoms. At $\frac{1}{3}$ ML of NO all silicon-surface states are passivated and this growth phase saturates. As a result there are no silicon states in the middle of the bulk band gap but the surface valence level is located above that of the bulk and the conduction-band edge is located below that of the bulk. Above $\frac{1}{3}$ ML of NO, a second higher-energy growth phase is possible in which each N_2 bonds on the tops of two oxygen atoms bridging them. This configuration becomes the most stable phase at a coverage of 1 ML NO. At this coverage we find that it removes all the states from the SiC silicon surface and thus leaves the bulk band-gap state free. We hope this work is useful for further experimental and theoretical studies on the growth and passivation of oxynitrides on the 4*H*-SiC (0001) surface.

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