

## Asymmetry of adsorption of oxygen at wurtzite AlN (0001) and (000 $\bar{1}$ ) surfaces: First-principles calculations

Honggang Ye,<sup>1</sup> Guangde Chen,<sup>1</sup> Youzhang Zhu,<sup>1</sup> and Su-Huai Wei<sup>2</sup>

<sup>1</sup>*Department of Applied Physics, Xi'an Jiaotong University, Xi'an, 710049, People's Republic of China*

<sup>2</sup>*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

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First-principles calculations are performed to study the adsorption of oxygen at wurtzite AlN (0001) and (000 $\bar{1}$ ) surfaces as a function of oxygen coverage. We find that the adsorption of oxygen at the AlN (000 $\bar{1}$ ) surface has a larger binding energy than at the AlN (0001) surface. The hollow site (H3) is preferred for the (0001) surface, whereas the site directly above the Al sublayer and the H3 site are almost degenerate in energy for the (000 $\bar{1}$ ) surface. The trend of the adsorption energy as a function of the oxygen coverage for the AlN (0001) surface is similar to that of GaN, whereas for the AlN (000 $\bar{1}$ ) surface it is different from GaN. The asymmetry of the oxygen adsorption at the two surfaces is explained using the electron counting rule and the resulting surface electronic states.

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Surface study is an indispensable subdiscipline of materials research.<sup>1</sup> A microscopic determination of semiconductor surface structures is crucial in understanding its material properties and can provide important guidance to tune material properties during crystal growth. AlN is one of the III-nitride semiconductors, which has great potential for high-power, high-temperature UV photoelectronic devices.<sup>2</sup> Some work has been done in the past to study AlN surface properties, such as surface reconstruction,<sup>3-7</sup> surface band structure,<sup>8</sup> and surface phonons.<sup>9,10</sup> Oxygen is one of the most abundant unintended impurities incorporated in crystal lattice or adsorbed at surface in III-nitrides. Unlike in GaN where O behaves as a shallow donor, it acts as a deep center in AlN due to the wide band gap of AlN.<sup>11</sup> Experimental studies have also shown that O adsorption at the AlN surface has effects on the surface roughness,<sup>12</sup> surface chemical stability,<sup>13</sup> surface contact with metal,<sup>14</sup> surface acoustic properties,<sup>15,16</sup> and thermal conductivity.<sup>17</sup> However, there is a lack of theoretical study of oxygen adsorption at the AlN surface. It is not clear where the stable oxygen adsorption site is and what is the dependence of the stability and surface electronic structures on the surface polarity and coverage.

In this work, we performed first-principles calculation to investigate the adsorption of oxygen at wurtzite AlN (0001) and (000 $\bar{1}$ ) surfaces, which are the two most common surfaces of all III-nitrides. We calculated the adsorption energies of various oxygen coverages at three possible adsorption sites. We show that the adsorption of oxygen at the Al-adlayer-terminated (000 $\bar{1}$ ) surface is more exothermic than at the AlN (0001) surface. The hollow site (H3) is preferred for the (0001) surface, whereas the site directly above the sublayer (T4) and the H3 site are almost degenerate in energy for the (000 $\bar{1}$ ) surface. Electronic structure calculations show that the calculated results can be understood using simple electron counting rules applied to these semiconductor surfaces.

The calculations are performed employing the general gradient approximation<sup>18</sup> within the first-principles density-functional theory. We used the plane wave basis and the

Vanderbilt ultrasoft pseudopotentials.<sup>19</sup> The energy cutoff for the basis function is 500 eV. A  $3 \times 3 \times 1$  Monkhorst-Pack mesh<sup>20</sup> is used to for the Brillouin zone integration. The supercells of  $2 \times 2$  units are built containing eight AlN bilayers in which the lower six bilayers were fixed in the bulk optimized configuration. The upper two bilayers and any adatoms or adlayers are allowed to fully relax by minimizing the quantum mechanical force on each ion to be less than 0.03 eV/Å. The vacuum thickness between two neighbor slabs is 10 Å. Test calculations using a supercell of ten AlN bilayers and 12.5 Å vacuum thickness yield almost identical results, indicating that the cell size is converged. To prevent unphysical charge transfer between the top and bottom slab surfaces, pseudohydrogens with fractional charges are used to saturate the dangling bonds in the bottom of the slabs.

Previous studies have shown that all group-III nitrides prefer cation terminated surfaces.<sup>21,22</sup> We considered here three possible adsorption sites, denoted as H3, T4, and atop. For the Al-terminated (0001) surface, they are shown in Fig. 1(a). For the N-terminated (000 $\bar{1}$ ) surface, we consider here a  $(1 \times 1)$  Al adlayer structure at the atop site [Fig. 1(b)], which is one of the stable surface configuration observed for AlN at Al-rich conditions.<sup>5,22</sup> We considered 0.25, 0.5, 0.75, and 1 ML (monolayer) of oxygen coverage located at each adsorption sites.

The adsorption energy is defined as

$$E_{ads} = \frac{1}{N} \left( E_{total} - E_{reference} - \frac{N}{2} E_{O_2} \right).$$

Here,  $N$  is the number of O atoms adsorbed on the AlN surface,  $E_{total}$  is the total energy of the oxygen adsorbed surface,  $E_{reference}$  is the total energy of the fully relaxed reference surface without oxygen, and  $E_{O_2}$  is the energy of an isolated  $O_2$  molecular.

Figure 2 shows the calculated lowest adsorption energies as a function of the oxygen coverage for both the (0001) and Al-adlayer-terminated (000 $\bar{1}$ ) surfaces. The adsorption positions are at H3 sites for both the surfaces. The large negative

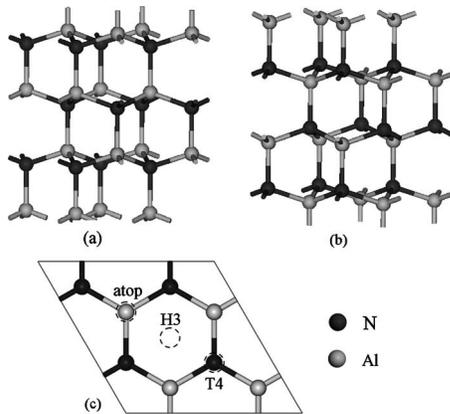


FIG. 1. Three dimensional views of the upper part of (a) the ideal (0001) surface, and (b) the Al-adlayer-terminated (000 $\bar{1}$ ) surface; (c) the top view of the (0001) surface and the possible adsorption sites are marked by dashed circles. H3 is the hollow site, atop is the site directly above the surface atoms, and T4 is the site directly above the sublayer (second layer) atoms.

adsorption energies shown in Fig. 2 suggest that the reactions between the O atoms and the surface atoms are strongly exothermic, especially for low coverage and at the (000 $\bar{1}$ ) surface. In the following, we will discuss in more detail the general trend of oxygen adsorption at the two surfaces.

For the AlN (0001) surface, the adsorption energies become less negative when the oxygen coverage increases from  $-6.6$  eV at 0.25 ML coverage to  $-2.6$  eV at 1 ML coverage, indicating strong repulsive interactions between the O adatoms. Therefore, with appropriate oxygen chemical potential, the adsorption of oxygen at this surface could favor low coverage situation. The shape of the solid line is similar to that found for GaN,<sup>23,24</sup> but the value of the adsorption energy is much larger, indicating that the AlN (0001) surface is easier to be oxidized than GaN. The O atoms preferentially adsorb at the H3 site of the AlN (0001) surface for all coverages. This is consistent with the results of Sun *et al.* for GaN,<sup>24</sup> but is inconsistent with the report of Zywiez *et al.*,<sup>23</sup> where the atop position is the preferential site when the oxygen coverage is above 0.5 ML.

The relaxed atom configurations with O atoms adsorbed

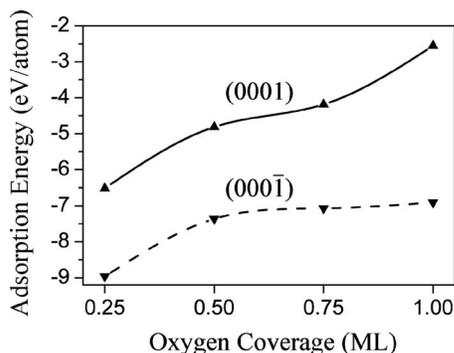


FIG. 2. Oxygen adsorption energies per O atom at H3 sites of (0001), solid line, and (000 $\bar{1}$ ), dashed line, surfaces.

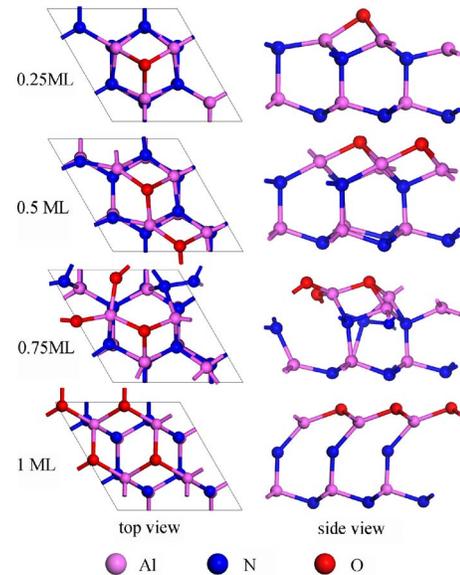


FIG. 3. (Color online) Top and side views of relaxed atom configurations with 0.25, 0.5, 0.75, and 1 ML oxygen coverages at H3 sites of the AlN (0001) surface.

at H3 sites of the AlN (0001) surface are shown in Fig. 3. At 0.25 ML coverage, the O adatom at the atop site is unstable and relax spontaneously to the H3 site. The adsorption energy of the O adatom at the T4 site is much smaller because there is a stronger electrostatic repulsion between the T4 O adatom and the nitrogen atom below.<sup>5,25,26</sup> When the oxygen coverage is above 0.5 ML, significant surface reconstructions occur. At 0.5 ML coverage, the O adatom is still threefold coordinated at the H3 site, but displaces away from the center. At 0.75 ML coverage, the strong displacement of the O adatoms at the H3 sites leads to alternating threefold and twofold O adatoms and to the formation of N-N below. When 1 ML oxygen covers all the H3 sites at the surface, these O adatoms and surface Al atoms form an Al-O bilayer, similar in structure to the original AlN bilayer, except for a displacement parallel to the surface. The formation of this Al-O bilayer breaks the Al-N bonds underneath making the surface N bond only to two Al atoms: one with the surface Al and one with Al in the next AlN bilayer. When large reconstructions occur, relaxing two bilayers may not be enough; we thus tested the results of 0.75 and 1 ML oxygen coverages by allowing three bilayers underneath the surface to relax. We find that the results are essentially unchanged.

For the Al-adlayer-terminated AlN (000 $\bar{1}$ ) surface, the magnitude of the adsorption energies decrease from 8.9 eV at 0.25 ML coverage to 6.9 eV at 1 ML coverage, but the variation is small when the oxygen coverage is above 0.5 ML, indicating a weak repulsion. **The large negative adsorption energy and weak repulsive interaction indicate that O atoms can easily and homogeneously adsorb at this Al-adlayer-terminated AlN (000 $\bar{1}$ ).** Compared with that of the Ga-adlayer-terminated GaN (000 $\bar{1}$ ) surface,<sup>23,24</sup> the adsorption energy of AlN is much larger because the Al-O bond is stronger than the Ga-O bond. The trend with increasing oxygen coverage is also different from GaN, for which the mag-

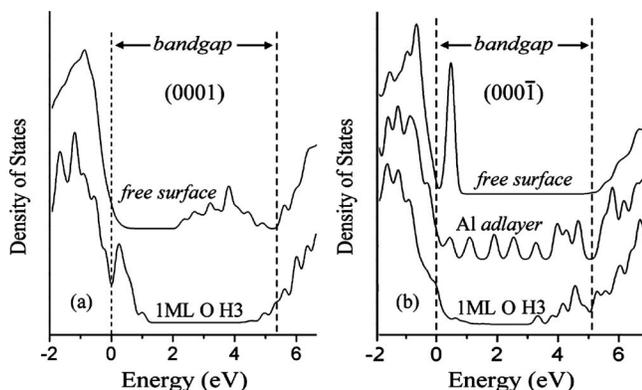


FIG. 4. Density of states (in arbitrary units) for the surface models: (a) AlN (0001) free surface and surface covered by 1 ML of oxygen; (b) AlN (000 $\bar{1}$ ) free surface, free surface with Al adlayer, and 1 ML of oxygen covered on Al adlayer. The dotted lines are VBM and CBM of bulk AlN.

nitude of the adsorption energy increases slightly with increasing oxygen coverage, indicating an attractive interaction between the O atoms on the GaN (000 $\bar{1}$ ) surface. This could be explained by noticing that the Al–O bond is more ionic and the O–O distance at the AlN (000 $\bar{1}$ ) surface is smaller than on the GaN (000 $\bar{1}$ ) surface, so the Coulomb repulsion between the O atoms is larger on the AlN (000 $\bar{1}$ ) surface than on the GaN (000 $\bar{1}$ ) surface.

For this Al-adlayer-terminated AlN (000 $\bar{1}$ ) surface, it is interesting to see that, unlike in the case for the AlN (0001) surface, oxygen adsorbed at both H3 and T4 sites is almost energetically degenerate, although it is still slightly lower at the H3 site for all the coverages. This is because for the Al-adlayer-terminated AlN (000 $\bar{1}$ ) surface, the environment surrounding the H3 and T4 sites are similar and O always bonds with Al below. We also calculated 1 ML of oxygen directly adsorbed at H3 sites of a N-terminated clean AlN (000 $\bar{1}$ ) surface. Its adsorption energy is  $-0.3$  eV, indicating that the Al adlayer has greatly improved the adsorption of oxygen at the AlN (000 $\bar{1}$ ) surface.

To help understand the calculated trend for O adatom stability under different coverages and surface orientations, we plot in Fig. 4 the calculated densities of states (DOSs) for some of the surfaces. For the donorlike AlN (0001) free surface, each Al has one dangling bond, which creates surface states near the bulk conduction band minimum (CBM). A

simple electron counting rule suggests that because each Al dangling bond contribute  $3/4$  electrons,  $3/8$  coverage of oxygen at the Al (0001) surface is needed to possibly passivate the surface, removing the dangling bond states. Further addition of oxygen to the surface will convert it into an acceptorlike surface, creating a dangling bond state near the bulk valence band maximum (VBM). These dangling bond states make the surface unstable, thus reducing the magnitude of the oxygen adsorption energy, and cause significant surface reconstruction at high oxygen coverage. For a 1 ML covered (0001) AlN surface, we find that the surface state is localized on the second layer N atoms, which becomes two-fold coordinated after the reconstruction. The transfer from the O dangling bond state to the N dangling bond state is consistent with the fact that O is more electronegative than N.

For an acceptorlike clean AlN (000 $\bar{1}$ ) free surface, a sharp peak of DOS of surface N atom states lies above the VBM. The Al adlayer can remove the sharp peak, but it also induces other surface states, now closer to the CBM, because each Al adatom has three dangling bonds. When a monolayer of oxygen is added above the Al adlayer, most of the states in the band gap are removed, except some residual states near the CBM. This is because, according to the electron counting rule, 1 ML of oxygen is not enough to passivate all the dangling bonds of the Al adlayer. This explains why O repulsion in the Al-adlayer-terminated (000 $\bar{1}$ ) is weak.

In summary, using first-principles method, we have examined oxygen adsorption at wurtzite AlN surfaces. We show that the adsorption of oxygen at AlN (0001) is very different from that at the Al-adlayer-terminated (000 $\bar{1}$ ) surface. The oxygen adsorption at the (000 $\bar{1}$ ) surface is expected to be much easier than at the AlN (0001) surface. The H3 site is the preferential site for the (0001) surface, and the T4 and H3 sites are almost degenerate in energy for the Al-adlayer-terminated (000 $\bar{1}$ ) surface. The trend of the adsorption energy as a function of the oxygen coverage for the AlN (0001) surface is similar to that of GaN, whereas for the AlN (000 $\bar{1}$ ) surface it is different from GaN. The observed trends are explained by analyzing the surface electronic states for these systems.

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