Density Functional Study of the First Wetting Layer on the GaN (0001) Surface

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ABSTRACT: The first wetting layer on the GaN (0001) surface has been investigated at the level of density functional theory. Many water adsorption models have been analyzed and it is observed that the number of water molecules that can be dissociated is limited to 0.375 ML of adsorption sites; further water dissociation will cost energy penalty. The coverage of hydroxyl groups on surface could be up to 0.75 ML instead. It is also observed that the additional charge on the surface will totally transfer to water adsorbates when the water dissociation number is 0.375 ML. Meanwhile, the surface states will disappear when all the adsorption sites are occupied by dissociated or intact water. All of these phenomena can be attributed to the electron counting rule of III–V semiconductor growth theory. We suggest that the electron counting rule could be generally applied to the water adsorption on polar III–V and II–VI semiconductor surfaces.

I. INTRODUCTION

In recent decades, the need for clean and renewable energy sources for our future has driven the investigations for sun light harvesting. Water splitting is one of those plausible processes, which only includes environmental harmless molecules. Except for the very first proposed catalyst, TiO2, the gallium nitride (GaN) related materials have been studied in experiments and theory for a very long time already because of its important applications in optoelectronic devices. Many efforts have been devoted to investigate the stabilities of GaN surfaces and its manufacture process. After years of experience, there are three general criteria for water splitting catalysts: (1) the band gap should be narrower than 3 eV for visible light adsorption; (2) the band-edge potentials must locate at positions allowing for the reduction and oxidation of water; and (3) the material has to be stable during photocatalytic reaction. In general, the intrinsic band gaps of GaN and other semiconductors are too large to harvest solar spectrum. Numbers of experiments have tested various doped GaN materials to tune the band gap width in order to improve visible light adsorption. The using of cocatalyst is also very common in experiments for improving the separation of photogenerated electrons and holes and also the overall efficiency. The using of cocatalyst is also very common in experiments for improving the separation of photogenerated electrons and holes and also the overall efficiency. Experiments with GaN in formations of wire, nanoparticles, and etched film have also been done in order to test the effect of increasing interaction area. To investigate the mechanism of water splitting processes at the water/interface, various experiments had been designed to achieve better understanding of the behaviors of photoexcited carriers such as electron hole recombination and photocurrent density.

Numbers of theoretical studies have estimated the gaps of the alloys in GaN related materials via density functional theory (DFT) to look for the best alloy combination for water splitting. However, there is still a lack of an atomic picture of water splitting process including the full picture of electron–hole pair excitation by photon adsorption, the process of water reduction and oxidation, and many other details. It might still be difficult to simulate the full water splitting process via the theoretical tools today; however, various works have been done to give some comprehension of the water splitting process or water/catalyst interface. Shen et al. investigated the water adsorption on the GaN (1010) surface by DFT calculations. They observed that water molecules will be dissociated on this surface with a tiny energy barrier of 1.6 meV. In another simulation by Shen with water sandwiched by a GaN slab, it was observed that 83% of GaN surface sites were occupied by dissociated water molecules. They had demonstrated that the first wetting layer on the GaN (1010) surface would be almost in dissociated water, even though the dissociation rate was not 100%. The reason for not achieving 100% dissociation could be the hindrance caused by the interaction between bulk water and adsorbates (they may form hydrogen bonds) or also the domain separation of the remaining Ga and N sites. To further dissociate water molecules, the proton hopping process in water molecules is needed and it may need to take a much longer simulation time than they did. In the same work, Shen et al.

Received: December 16, 2012
Revised: April 3, 2013
Published: April 4, 2013
al. also suggested the plausible proton-coupled electron transfer (PCET) steps by using cluster models. Their work is important for giving the plausible pictures and estimating the photon energy absorbed of water splitting process on the GaN (1010) surface. However, the energy estimation of excited states may not be accurate by using DFT method and also using a small GaN cluster model to mimic the surface; a more accurate simulation method and realistic model should be used to achieve results more close to experimental observations.

On the other hand, P.-T. Chen et al. investigated the dissociation of a water molecule on GaN (0001) and (0001) surfaces via DFT calculations. They found that it is feasible for water to dissociate into Ga(N)−OH and Ga(N)−H groups on both surfaces under room temperature. However, the generation of one H2 molecule was suggested to happen on (0001) only, but not on (0001) surface. Meanwhile, Tan et al. used molecular dynamics (MD) simulations with an empirical force field to study the density, dipole distribution, drift velocity, and vibration spectrum of interface water at the GaN (0001) surface. Tan tried to provide the important information of water’s behavior near the GaN (0001) surface with a nondissociated SPC water model including a flexible extension and a fixed GaN (0001) surface model. However, the GaN surface wetted with dissociated water was not considered in Tan’s work and more efforts are therefore needed to model the GaN surface one step closer to realistic cases.

Because GaN (0001) is one of the most important surfaces in the GaN growing process today, we will present our effort in the investigation of multwater-molecule adsorption on the GaN (0001) surface in this paper. Our study will also provide more information to clarify the discrepancy of the results between the former DFT and MD works.27−29

II. METHOD AND CALCULATION DETAILS

The GaN (0001) surface is modeled by a slab containing 4 × 4 × 3 unit cells (shown in Figure 1) with a 20 Å vacuum in z direction. So there are six double atomic layers included in the GaN slab. The original hexagonal supercell is reshaped into an orthorhombic cell with experimental lattice constants. That is, the lengths of three supercell vectors a, b, and c are 12.76, 11.05, and 35.57 Å. The dangling nitrogen atoms at (0001) surface are passivated with pseudohydrogen atoms with 0.75 e. The positions of those pseudohydrogen atoms are determined by optimizing their coordinates with a fixed pristine GaN slab. Once the positions of pseudohydrogen atoms are decided, all pseudohydrogen atoms and also the bottom four of six GaN double layers are fixed during structure optimization in all the water adsorption models.

All of the calculations are performed using DFT, which is implemented in the Vienna ab initio simulation package (VASP). The electron wave functions are solved with plane-wave basis set in conjunction with pseudo potentials by the projector augmented-wave (PAW) method. Electron exchange-correlation energies are treated with Perdew–Wang 91 (PW91) generalized gradient approximation. The 4s, 4p, 3d orbitals of Ga atoms, 2s, 2p orbitals of N and O atoms, and 1s orbital of H atoms are regarded as valence electrons in all calculations. A 3 × 3 × 1 Γ-centered Monkhorst-Pack k-point mesh and 400 eV energy cutoff are used to make sure the adsorption energies are well estimated. Force on each atom is requested to be less than 0.01 eV/Å for the global break condition during structure optimization. Because in our GaN slab model there is a net dipole in the [0001] direction, which will introduce artificial electric field in calculations with periodic boundary conditions (PBC), the dipole correction scheme introduced by Neugebauer and Scheffler is applied in all calculations except for the GaN bulk system.

The total adsorption energies of all water adsorption models are calculated by eq 1.

\[ E_{ad} = -(E_{total} - E_{sur} - m \times E_{water}) \tag{1} \]

where \( E_{total} \), \( E_{sur} \), and \( E_{water} \) are the total energy of water adsorption system, the optimized GaN (0001) surface, and optimized one water molecule; \( m \) is the number of water molecules adsorbed in the system. The optimized GaN (0001) surface refers to the (2 × 1) reconstructed surface, which is 0.06 eV/Ga lower than flat (1 × 1) surface in our calculation.

We have also applied Bader’s method to analyze the charge distribution of GaN slab and water adsorbates.40 Eq 2 shows how we calculate the charge transfer of each GaN double layer and the adsorbates (water molecules, H or OH groups)

\[ \rho^{gain}_{\text{double layer/adsorbate}} = \rho^{double layer/adsorbate} - m \times \rho^{GaN/water} \tag{2} \]

where \( \rho^{double layer/adsorbate} \) is the charge of one GaN double layer or the adsorbates layer via Bader charge analyses; \( \rho^{GaN/water} \) is the charge of one GaN pair or one water molecule, which is eighteen or eight, respectively; and \( m \) is the equal number of GaN pairs in one double layer (it is sixteen in our models) or water molecules in adsorbates.
III. RESULTS AND DISCUSSION

A. Clean GaN (0001) Surfaces. Kempisty et al. 43 demonstrated the (2 × 1) surface reconstruction of GaN (0001) surface is more stable than the flat (1 × 1) surface by about 0.08 eV/Ga via DFT calculations. Figure 1a,b shows the optimized side views and top views of the (1 × 1) and (2 × 1) GaN (0001) surfaces, respectively. The (2 × 1) surface is characterized by top Ga-atom rows in alternatively high and low z positions. In our calculation, the (2 × 1) surface energies than the (2 × 1) to (1 × 1) GaN (0001) surfaces, respectively. The (2 × 1) surface is a newly discovered surface reconstruction in theory; there is no experimental evidence yet. We are aware of it being possible to find out other types of surface reconstructions with lower surface energies than the (2 × 1) surface in theoretical calculations when a larger surface model is used. The finding of the most stable GaN (0001) surface is going to affect the reference point of total adsorption energies in eq 1. However, because the focus of this work is the character of the first wetting layer on the surface, we did not make more effort to find out other possible surface reconstructions.

The creation of the surface will not just create surface states, modifying the electron structure, but also redistribute the electron density in each double layer. In Figure 2, we show the density of states (DOS) of GaN bulk and two (0001) surfaces. The Fermi level of each system is indicated with the triangle mark in the same color of its DOS curve.

![DOS of GaN surfaces](image)

**Figure 2.** DOS of GaN bulk and two (0001) surfaces. The Fermi level of each system is indicated with the triangle mark in the same color of its DOS curve.

In Table 1, we present the electron gain of each double layer of two surfaces relative to bulk by Bader analysis; the electron gain of the (1 × 1) surface model without pseudo H atoms is also given in the third row. As indicated in the third row, the creation of surfaces will cause the electron to accumulate at the Ga-terminated (0001) surface and disperse at the N-terminated (0001) surface when comparing with GaN bulk values (it is 18 eV for each Ga–N pair). The introduction of the pseudo H atoms will greatly improve the charge distribution in the fifth double layer to be more bulk-like (electron gain close to zero); however, it makes the first two surface double layers carrying more electrons. This is reasonable because when there is no pseudo H atom, the electron depletion and accumulation zones at (0001) and (0001) surfaces will attract each other and let partial electron at the two zones compensate each other. The electron gain in the sixth double layer has different signs between models with and without pseudo H atoms because the pseudo H atoms offer electrons to the bottom nitrogen atoms in the sixth double layer of the corresponding model. By analyzing the details of electron gain of each atom, it is found that the surface Ga atoms possess different electron number between lower and higher row in the (2 × 1) surface model. Each Ga atom in lower row possesses 0.31e fewer than the average of surface Ga atoms of the (1 × 1) surface, atom in higher row is 0.28e more when GaN slab passivated with pseudo H atoms. Because our study focus is on the (0001) surface, we add pseudo H atoms to terminate the dangling bonds at (0001) surface for all calculations of water adsorption in order to make the electron gain in the deeper double layers converging to bulk value. The use of pseudo H atoms also helps the convergence of electron self-consistent field (scf) calculations.

We also test the convergence of surface energies and electron gain in each double layer when the number of double layers is increased. By testing two surface models with 8 and 10 double layers, we find that the surface energies will vary within 0.014 eV/Ga and 0.03e for electron gain in each of the top four double layers. In the later section, it is observed that the major contribution of electron transfer to water adsorbates is from the top two double layers. Hence, six double layers should be enough for our investigations on the first wetting layer on GaN (0001) surface.

### Table 1. Electron Gain of Each GaN Double Layer Relative to Bulk Value

<table>
<thead>
<tr>
<th></th>
<th>first</th>
<th>second</th>
<th>third</th>
<th>fourth</th>
<th>fifth</th>
<th>sixth</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 × 1)</td>
<td>5.167</td>
<td>0.649</td>
<td>-0.237</td>
<td>-0.019</td>
<td>-0.026</td>
<td>3.318</td>
</tr>
<tr>
<td>(2 × 1)</td>
<td>5.257</td>
<td>0.557</td>
<td>-0.250</td>
<td>-0.014</td>
<td>-0.021</td>
<td>3.323</td>
</tr>
<tr>
<td>(1 × 1)/wo-H</td>
<td>5.014</td>
<td>0.604</td>
<td>-0.245</td>
<td>-0.018</td>
<td>-0.258</td>
<td>-5.096</td>
</tr>
</tbody>
</table>

The GaN double layers are counting from the top to the bottom, as depicted in Figure 1a. The unit is in e.
models of intact water, dissociated water, and H₂ production plus one oxygen adatom, respectively. Figure 3a–c shows the
top views of these three states of four-water molecule adsorption. As indicated in Figure 3, the adsorption of one
intact water molecule occupies one Ga site, one dissociated water occupies two Ga sites, and one oxygen adatom occupies
three Ga sites. Our results of the adsorption energies and relative energies per water molecule of three stable adsorption
states (labeled as states 1, 2, and 3) for one-, two-, and four-water-molecule adsorption are listed in Table 2. Because our
model surface has a 4 × 4 cross-section in the x–y plane, P.-T. Chen’s models have the same adsorption density as our four-
water-molecule adsorption models, and the results are in good agreement with a difference smaller than 0.15 eV/H₂O.
Actually, the oxygen atom of the hydroxyl group in state 2 could bond to two Ga sites and lower the total energy like those state 2 behaving in one- and two-water-molecule adsorption systems. However, when water adsorbates become
crowded on the surface, almost each hydroxyl group occupies one Ga site only as depicted in Figure S1 of the Supporting
Information.

In Table 2, the adsorption energies for one- and two-water-molecule adsorption are all higher than corresponding four-
water molecule absorption states with various values. The reasons for the higher adsorption energies in lower water
adsorption density could be resulted from the different patterns of surface reconstruction in our models or special adsorption
pattern under periodic boundary condition with/without hydrogen bonds included; however, we did not test more models with different Ga adsorption sites and are not going to discuss this point in this work. Even though it is also important
to investigate the mechanism of how the surface adsorbs water molecules at very low density, in the following paragraphs we
will just focus on the general features of the first wetting layer on the GaN (0001) surface, which will be more relevant to the
real water splitting experimental environment.

C. Water Adsorption in Higher Density to the First
Wetting Layer. To investigate the first wetting layer on the GaN (0001) surface, we have optimized models of water
adsorption with a combination of intact and dissociated water adsorption forms. The state with H₂ production and one
oxygen adatom is not considered since the oxygen adatom occupies three Ga-site sites without accordingly increasing the
total adsorption energy in the low density water adsorption calculations. For simplicity, we use symbol mw_n to indicate an
adsorption category having m water molecules adsorbed with n dissociated molecules in the following paragraph. That is, 8w_0
means eight water molecules adsorbed on surface with all molecules in intact form; 8w_3 means eight water molecules
adsorbed with three molecules dissociated and five in intact form. We do not specify the name of a certain adsorption
model because most of the time we will just focus on the overall adsorption behavior; but the feature of some individual
adsorption models will be mentioned whenever it is necessary.

Tables 3 and 4 list the total adsorption energies and adsorption energies per water molecule of all the models we have
calculated. Some entries contain two or three numbers if we build different models for the same category. Each row
contains the data of different water adsorption density; the column index indicates the number of dissociated water
molecules. That is the adsorption energy of mw_n is at the (m,n) entry. Because the total number of Ga sites is sixteen in
our simulation slab, the maximum number of water dissociation is eight. A mw_n adsorption model has m + n Ga sites occupied by m – n intact water and n dissociated water. The entries with n larger than m and m + n larger than 16 are not available for
 constraints of a dissociable number of water molecules or total Ga-site number. Besides that, some entries are empty if we did
not build a model for it; however, we believe the data we have should be sufficient to demonstrate the phenomena we
observed. We have tested more than one model for some adsorption categories and the energy variation between models
could be as large as 0.7 eV. The top views of all water adsorption systems are plotted in Figure S1 of the Supporting
Information for readers who are interested in the details. The arrangements of water adsorbates between some systems do
have a relationship like one more water molecule dissociated or adsorbed in between, but we randomize the position of those
actions. In addition, we build two sets of eight-water-molecule adsorption in most cases with one in high and the other one in
low symmetry; the 9w_n, 10w_n, and 11w_n (n not equal to 0) systems are not related to those 8w_n systems. After these
efforts, we find that there is an obvious hierarchy between different adsorption categories, as clearly shown in Table 3.

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Table 2. Adsorption Energy and Relative Energy (Given in Parentheses) per Water Molecule of One, Two, and Four
Water Molecules Adsorbed on the GaN (0001) Surface

<table>
<thead>
<tr>
<th>state</th>
<th>1 H₂O</th>
<th>2 H₂O</th>
<th>4 H₂O</th>
<th>P. T. Chen’s result</th>
</tr>
</thead>
<tbody>
<tr>
<td>state 1</td>
<td>1.20 (0)</td>
<td>1.32 (0)</td>
<td>0.99 (0)</td>
<td>1.05 (0)</td>
</tr>
<tr>
<td>state 2</td>
<td>2.63 (−1.43)</td>
<td>2.67 (−1.35)</td>
<td>2.42 (−1.43)</td>
<td>2.27 (−1.22)</td>
</tr>
<tr>
<td>state 3</td>
<td>1.65 (−0.45)</td>
<td>1.51 (−0.19)</td>
<td>1.37 (−0.38)</td>
<td>1.32 (−0.27)</td>
</tr>
</tbody>
</table>

*States 1, 2, and 3 correspond to the three stable states: intact water, dissociated water, and H₂ production plus oxygen adatom,
respectively. The numbers are given in eV.*
In Table 3, it is observed that the total adsorption energy in the same row is monotonically increasing up to six molecules dissociated; however, it always has a great decrease when the dissociation number increases from six to seven. The adsorption energy reduces further when the dissociation number goes from seven to eight (compare 8w_7 and 8w_8). This means the GaN surface has limited ability to dissociate water; six seems to be the maximum number for dissociable molecules, and further dissociation will result in a penalty in total adsorption energy. In terms of the surface coverage, the maximum dissociation will be 0.375 ML (6/16 ML). After six water molecules dissociated on GaN surface, further water adsorption in intact form can keep increasing total adsorption energy. 10w_6 has the largest adsorption energy in our models, which has 10 water molecules adsorbed with 6 of them dissociated.

It is observed in the first column of Table 4 that the intact form adsorption could contribute to average adsorption energy at 1.0 to 1.1 eV up to 10 water molecules adsorbed. The structure optimization with more than eleven intact water molecules adsorption did not converge successfully in our trials; those trial systems would evolve into systems with some water molecules dissociated or moving out of the first wetting layer. In addition, when there are seven or eight water molecules dissociated, the model systems possess partial magnetization; the magnitude is 0.17 to 0.4 $\mu_B$ for seven water molecules dissociation and 0.84 to 0.9 $\mu_B$ for eight water molecules dissociation. The partial magnetic moment is mainly concentrated on those oxygen atoms of hydroxyl groups. Because the systems with seven and eight water molecules dissociation are very unfavorable in total energy, these systems may not appear in experiments in low temperature and with well controlled humidity that water adsorption is not thicker than one molecule layer.

**D. Electron Transfer.** According to eq 2, we can quantify the electron transfer between GaN slab and water adsorbates (water in intact form or dissociated form). The results are summarized in Figure 4 with the electron gain of water adsorbates multiplied by a minus sign. We use the average value for categories with more than one model. In Figure 4a, it is observed that electrons will transfer from the GaN slab to water adsorbates with a major contribution from the first top double layer and a minor part from the second double layer. In all simulation models, the deeper double layers other than the first two top ones contribute negligible electrons to water adsorbates. To verify this point, we have tested several 8w_n systems with 8 and 10 GaN double layers (without the structure optimization of adsorbates) and observed the same phenomena. The variation of electron gain in first two double layers and water adsorbates are within 0.3 e. The sum of electron transferred from the third and deeper double layers is smaller than 0.08 e in all models.

The horizontal lines in Figure 4a,b represent the minus sum (5.81 e) of the electron gain from the first two double layers relative to GaN bulk (see Table 1). It is observed that when there are more than seven water molecules dissociated, water adsorbates will gain more than 5.81 electrons. The model 10w_6 with the highest total adsorption energy acquires 5.89 e.

In Table 3, it is observed that the total adsorption energy in the same row is monotonically increasing up to six molecules dissociated; however, it always has a great decrease when the dissociation number increases from six to seven. The adsorption energy reduces further when the dissociation number goes from seven to eight (compare 8w_7 and 8w_8). This means the GaN surface has limited ability to dissociate water; six seems to be the maximum number for dissociable molecules, and further dissociation will result in a penalty in total adsorption energy. In terms of the surface coverage, the maximum dissociation will be 0.375 ML (6/16 ML). After six water molecules dissociated on GaN surface, further water adsorption in intact form can keep increasing total adsorption energy. 10w_6 has the largest adsorption energy in our models, which has 10 water molecules adsorbed with 6 of them dissociated.

**Table 3. Total Adsorption Energy of Water Adsorption Models**

<table>
<thead>
<tr>
<th>adsorbed number</th>
<th>dissociated number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1.20</td>
</tr>
<tr>
<td>2</td>
<td>2.64</td>
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<tr>
<td>3</td>
<td>3.66</td>
</tr>
<tr>
<td>4</td>
<td>3.97/4.48</td>
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<tr>
<td>5</td>
<td>6.21</td>
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<td>6</td>
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<td>7</td>
<td>7.86</td>
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<tr>
<td>8</td>
<td>8.94</td>
</tr>
<tr>
<td>9</td>
<td>9.74</td>
</tr>
<tr>
<td>10</td>
<td>10.2/10.4</td>
</tr>
<tr>
<td>11</td>
<td>17.6</td>
</tr>
</tbody>
</table>

The numbers are given in eV.

**Table 4. Adsorption Energy per Water Molecule of Water Adsorption Models**

<table>
<thead>
<tr>
<th>adsorbed number</th>
<th>dissociated number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1.20</td>
</tr>
<tr>
<td>2</td>
<td>1.32</td>
</tr>
<tr>
<td>3</td>
<td>1.22</td>
</tr>
<tr>
<td>4</td>
<td>0.99/1.12</td>
</tr>
<tr>
<td>5</td>
<td>1.24</td>
</tr>
<tr>
<td>6</td>
<td>1.15</td>
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<td>1.12</td>
</tr>
<tr>
<td>9</td>
<td>1.18</td>
</tr>
<tr>
<td>10</td>
<td>1.02/1.04</td>
</tr>
<tr>
<td>11</td>
<td>1.60</td>
</tr>
</tbody>
</table>

The numbers are given in eV.
additional electron in the horizontal line in (a) and (b) is adsorption with their total adsorption energy. The value of the horizontal line in (a) and (b) is $-5.8 \text{ e}$, which is the minus of the total additional electron in the first two double layers of the $(2 \times 1)$ surface.

Figure 4. Electron gain of water adsorbates and each GaN double layer. The GaN double layers are counted from the top of the surface, as depicted in Figure 1a. (a) The comparison chart of selected models in our calculations. (b) The electron gain chart of 8 water molecules adsorption with their total adsorption energy. The value of the horizontal line in (a) and (b) is $-5.8 \text{ e}$, which is the minus of the total additional electron in the first two double layers of the $(2 \times 1)$ surface.

electrons from the GaN slab, which is slightly more than the value of the horizontal line. When considering both the results of Table 3 and Figure 4a together, we suggest that the ability of dissociating water is strongly restricted by the electrons that could be offered from the GaN slab.

Figure 4b shows only the electron transfer of eight-water-molecule adsorption with the corresponding total adsorption energy. It is clear that the electron transfer increases almost linearly with increasing dissociated water number up to six molecules; the curve slope is reduced for the seventh and eighth water molecule dissociation. On the other hand, the increasing of total adsorption energy is also almost linearly proportional to the number of dissociated water molecules, up to six, in Figure 4b; however, the curve slope changes sign at the seventh water molecule dissociation and adsorption energy reduces more at the eighth water molecule dissociation. This phenomenon again suggests that the GaN (0001) surface could dissociate water up to six molecules without difficulty; further dissociation is disadvantageous for the surface extracted out too much electrons.

E. Density of States. Figure 5a–d shows the PDOS of several selected water adsorption models, bulk, and surfaces. The $k$-point mesh is increased to $9 \times 9 \times 1$ for all DOS calculations of the GaN surface systems; a $15 \times 15 \times 15$ $k$-point mesh for bulk. To compare the DOS shape of adsorption systems with bulk and clean surfaces, we match the positions of the two deepest PDOS peaks of bulk and of the fourth double layer of each surface system. Figure 5a shows the peaks position matching of selected systems; the two insets show the zoom in of PDOS around the two deepest peaks and Fermi level. Overall, the positions of the two deepest peaks around $-15.1$ and $-13.4 \text{ eV}$ can be matched really well among these models. With the same energy alignment of Figure 5a, Figure 5b,c shows the PDOS of the top four GaN double layers of different adsorption models and also DOS of GaN bulk. Figure 5d shows the PDOS of water adsorbates in models. For clear presenting, the PDOS curves are spaced by 40 vertically in Figure 5b,c, and spaced by 5 or 10 in Figure 5d. In Figure 5b,c, we observe that when there are more Ga sites occupied, the amount of surface states in PDOS will reduce correspondingly. When all of the Ga sites are occupied (like $10w_6$), these surface states in PDOS would all disappear and leave a parabola shape shoulder at the bottom of the conduction band edge as bulk DOS.

According to PDOS curves, the adsorption systems could be classified into three groups, $n$-doped, neutral, and $p$-doped. The PDOS of each calculated $11w_n$ model shows that the surface is slightly $n$-doped with the Fermi level shifting to a position a little above the original conduction band edge. On the other hand, when the adsorbed water molecules number is smaller than 10 and dissociation number is smaller than or equal to 6, the position of Fermi level will fluctuate among the surface states. However, when there are more than six water molecules dissociated, the Fermi level shifts to a position slightly beneath the top edge of the original valence band; that is, the surface becomes slightly $p$-doped.

In Figure 5d, it is observed that some peaks of water adsorbates PDOS will be close to or even slightly higher than 0 eV, which is about the top edge of the original GaN valence band. Those peaks are actually contributed from the hydroxyl groups on Ga sites without accepting any hydrogen bonds from other water adsorbates. The PDOS peaks of other hydroxyl groups will locate at lower energy like the $10w_6$ curve in Figure 5d. The PDOS contribution of water adsorbates in intact form will locate even lower in energy like the $4w_0$ curve.

F. Electron Counting Rule. Many theoretical studies of the GaN (0001) surface were focusing on the growth mechanism of GaN along the [0001] direction in experiments. $^{7-9,44,45}$ Besides the adsorption of ammonia molecules and Ga atoms, hydrogen atom adsorption was also extensively studied via DFT calculations. $^{43,46}$ It was concluded that the adsorption of ammonia molecules and hydrogen atoms follows the electron counting rule on the (0001) surface. $^{47,48}$ To be noted, the electron number mentioned in this section is different from what we get in Bader analysis; it is always some integer or fraction number of electrons that may participate in one chemical bond or fill some empty orbital.
Except for the valence electrons involved in the chemical bonds with bulk nitrogen atoms, each surface Ga atom will have $3/4$ electrons to partially fill those dangling bonds of surface Ga atoms. In our simulations, the $4 \times 4$ GaN surface has 16 Ga sites, which have 16 dangling bonds and 12 surface electrons available in total for those partially filled dangling bonds. According to the electron counting rule, the maximum number of chemical bonds formed with Ga dangling bonds on our surface model is 12 and then the surface leaves four empty 4sp$^3$ orbitals. At the same time, those empty orbitals are also able to accept the docking of electron lone pairs from water molecules (i.e., forming a dative bond) or filled with electrons from somewhere else. In our calculations, forming a dative bond between intact water and the GaN surface will lower the total energy by about 1.0 eV on average; the formation of chemical bonds will further lower total energy much more until all 4sp$^3$ orbitals are occupied by electrons. The formation energy of a dative bond is much stronger than Van de Waals force between molecules and usually larger than hydrogen bonds. In Figure S2 of the Supporting Information, we show the charge density distributions of an ammonia–borane pair, a water–borane pair, 1w_0, and 1w_1 to demonstrate the bonding in 1w_0 system is a typical dative bond.

When one water molecule is dissociated on the surface, two surface electrons will participate in the two new forming Ga–O and Ga–H chemical bonds. For a $m$w$_n$ system, there will be $12-2n$ surface electrons left not involved in chemical bonds, which will fill $6-n$ surface Ga 4sp$^3$ empty orbitals or other orbitals with higher energy. At the same time, there are only $16-m-n$ Ga sites left unoccupied by water adsorbates. It is easy to infer that if $m$ is larger than 10, $6-n$ will be larger than $16-m-n$. Hence, those surface electrons not participating in chemical bonds will fill either some 4sp$^3$ orbitals or some other higher energy orbitals when $m$ is either smaller or larger than 10. The systems with 10 water molecules adsorbed will make all Ga 4sp$^3$ orbitals filled by electrons in chemical bonds, lone pairs from water, or just the surface electrons from surface Ga atoms. Systems with $m$ smaller than 10 will have $10-m$ Ga 4sp$^3$ orbitals unfilled. On the other hand, if $n$ is 7 or 8, $12-2n$ will be a minus number, which means water adsorbates will acquire more than 12 surface electrons for forming chemical bonds and result in the first two top GaN double layers losing additional electrons. These systems always are much more unfavorable than those with six water molecules dissociation (see Table 3), because the electron of the Ga–N chemical bonds in GaN slab is extracted out.

For the systems with $m$ water molecules adsorbed (the $m$ row in Table 3), all have the same number of unfilled Ga 4sp$^3$ orbitals, but systems with more chemical bonds will have lower total energies when the dissociated water molecules are fewer
than six. For the systems with \( n \) water dissociated (the \( n \) column in Table 3), more intact water adsorbed will make more Ga 4sp\(^3\) orbitals to be filled by water lone pairs and lower the total energy up to 10 water molecules adsorbed. The system with the largest total adsorption energy, 10w\(_6\), forms 12 chemical bonds by dissociating 6 water molecules and accepting the docking of 4 intact water molecules on the surface. The 11w\(_5\) systems make all Ga 4sp\(^3\) orbitals full but did not further lower the total adsorption energy compared with the 10w\(_5\) system. This is because in each 11w\(_5\) system there are two electrons filling an orbital higher than Ga 4sp\(^3\).

The evolution of PDOS of GaN slab in Figure S5b,c could also be analyzed with the help of the electron counting rule. For systems with seven or eight water molecules dissociated, their PDOS indicates the surface is slightly p-doped. It can be explained as the water adsorbates extract too many electrons out and make the electron depletion in the GaN slab. On the other hand, the systems with eleven water molecules adsorbed show slightly n-doped because there are two more electrons filling an orbital higher than Ga 4sp\(^3\). For other systems, if there is one Ga 4sp\(^3\) orbital filled with unpaired surface electrons, there will be a surface state peak in PDOS with an area of two electrons between the Fermi level and the original valence band edge. If there is one Ga 4sp\(^3\) orbital empty, there will be an additional surface state peak in PDOS with an area of two electrons above the Fermi level. In other words, before water adsorption, there are 12- and 20-electron surface state peaks in PDOS of clean GaN slab below and above the Fermi level. When one intact water molecule adsorbed, the two-electron surface states above the Fermi level are removed; when one water molecule dissociated, both two-electron surface states below and above the Fermi level are removed.

Based on the above discussions, we suggest that at low temperature and well-controlled humidity the first wetting layer of water on GaN should be partially dissociated. If we count the four most stable models (9w\(_6\), 10w\(_5\), 10w\(_6\), 11w\(_5\)) as the most relevant conditions in experiments, the dissociation rate will be around 45–67\%. That means the real case is at the middle between fully dissociated and fully undissociated. However, the effect of hydrogen bonds from bulk water to the first wetting layer may affect the dissociation rate and it will need more effort to clarify.

**G. Water Adsorption beyond the First Wetting Layer.** In real experiments, the photocatalyst is embedded in liquid water for the overall water splitting reaction. Many hydrogen bonds will form between bulk water and the first wetting layer. In order to get some hints of the strength of hydrogen bonds and how bulk water may affect the DOS of GaN surface, we put one more water molecule on top of the first wetting layer systems. In total, we have tested systems of 7w\(_6\), 7w\(_7\), 8w\(_6\), 8w\(_7\), 8w\(_8\), 9w\(_6\), 9w\(_7\), 10w\(_0\), 10w\(_5\), 10w\(_6\), 11w\(_4\), and 11w\(_5\). The increased total adsorption energy ranges from 0.16 to 0.89 eV and it is 0.5 eV on average. There is no obvious rule for the strength of hydrogen bonds formed between the additional water molecule and the first wetting layer but, it can be concluded that the strength of hydrogen bonds is comparable with the energy difference between the adsorption of one intact and one dissociated water molecule. On the other hand, the PDOS of the GaN slab does not vary too much before and after one more water molecule adsorbed.

Bermudez and Long observed water adsorbed dissociatively on the GaN (0001) surface with a saturation coverage of 0.45–0.46 ML.\(^53\) Lorenz et al. observed a saturation coverage of \( \sim 1 \) ML instead.\(^52\) Both experiments are done near room temperature with gradually increasing water exposure up to \( \sim 10 \) and 30 L. Both experiments did not agree well with each other and differ from our result, 0.375 ML, in previous sections. There could be many experimental factors that we did not consider in previous sections responsible for divergent results like temperature, humidity level, surface condition, and so on. Temperature is one of the factors we try to compensate for by making the following assumptions. It is reasonable to assume when the temperature is high enough, hydrogen molecules could be released and leave far from surface. We calculate the adsorption energies of 9–16 hydroxyl groups on the GaN (0001) surface by eq 3.

\[
E_{ad} = -\left( E_{\text{total}} - E_{\text{sur}} - m \times E_{\text{water}} + \left( \frac{m}{2} \right) \times E_{H_2} \right)
\]

where \( m \) is the number of hydroxyl groups and \( E_{H_2} \) is the total energy of one hydrogen molecule. The results are presented in Table 5. It is observed that the total adsorption energy meets the maximum at 12-hydroxyl group adsorption and then reduce monotonically. The most stable hydroxyl group coverage is 0.75 ML (12/16 ML), which exactly meets the saturation coverage of component B in experiments done by Lorenz et al.\(^52\) So we suggest that the component B in the data of the experiment done by Lorenz et al. should be contributed by hydroxyl groups. We do not have a clue yet what results in component C in their experiment.

Önsten et al.\(^53\) observed triangular patterns on the ZnO (0001) surface before and after exposure to water with introducing the theoretical study by Kresse et al.\(^54\) for an explanation of their observations. Kresse et al. used the idea equivalent to the electron counting rule to construct the ZnO (0001) surface models and adsorption models of OH groups and O and H atoms, even though they did not use the terminology, electron counting rule. They predicted that the coverage of OH and H adsorption should be 0.5 ML while 0.25 ML for O adatoms. Although there is no experimental evidence yet to prove the electron counting rule should apply to the water or hydroxyl groups adsorption on the ZnO (0001) surface, we still would like to suggest that the electron counting rule can be commonly applied to the water adsorption on polar III–V and II–VI semiconductor surfaces.

**H. Corrections from Zero-Point Energy, Introduced Strain, and Simulation Method.** The zero-point energy of water adsorbates on metal surface can play an important role in the adsorption pattern.\(^55\) To estimate the zero-point energies, we calculate the phonon frequencies of water adsorbates on surface with a reduced GaN slab model. The reduced GaN slab is composed of 2 \( \times 2 \times 3 \) unit cells with a 20 Å vacuum in the \( z \) direction. There are only four Ga surface sites that can adsorb or dissociate water molecules. The results are presented in Table S1 in Supporting Information and it is observed that zero-point energy corrections will stabilize dissociated water by 0.1 eV relative to intact water. The wetting behavior on the
GaN (0001) surface will not change with the corrections from zero-point energies.

The applied strain usually will alter the chemical properties of the surface. However, it is an unavoidable factor that usually will be introduced in simulation from many aspects like lattice constants chosen, k-point mesh, modeling size, exchange-correlation functional, and so on. Those parameters will also affect bulk band gap in different levels. The size of the band gap is important to the GaN (0001) surface because water adsorption and dissociation involve the stabilizing of surface state electrons. We examine the difference resulting from the lattice constants used and the type of exchange-correlation functional with the reduced GaN slab model. The results are presented in Tables S1 and S2 in Supporting Information. The discrepancy between using experimental and DFT optimized lattice constants is small. In most water adsorption cases, the adsorption energies are decreased by 0.01 to 0.02 eV when optimized lattice constants are used. Only the 2w_2 system may have an adsorption energy with larger discrepancy by 0.09 eV. These results imply that the corrections from strain effect should be less than 0.1 eV for most systems of a GaN slab with 4 × 4 × 3 unit cells between using experimental or optimized lattice constants. About 0.4 eV discrepancies for systems with more dissociated water molecules.

Since the structure optimization using Heyd–Scuseria–Ernzerhof (HSE06) exchange-correlation functional is time-consuming, we adopted the optimized structures from the Perdew–Burke–Ernzerhof (PBE) calculations for the corresponding HSE06 calculations with α value of 0.3 as Mose et al. did. The bulk band gaps are 3.45 and 3.29 eV for using experimental and optimized PBE lattice constants, respectively, when an 8 × 8 × 6 k-point mesh and a 400 eV energy cutoff are applied. The gap between surface states and bulk original valence band edge is enlarged as well. Correspondingly, the adsorption energies in calculations with using HSE06 are larger than those using PBE and PW91. However, the wetting behavior on the GaN (0001) surface still obeys the electron counting rule, except for the charge transfer not quite matching the observation in Figure 4. The sum of additional surface charge does not match well with the electron gain when there is 0.75 ML chemical bonding coverage (3OH) in Figure S4 of Supporting Information. The PDOS shown in Figure S3 of Supporting Information follow the same evolution rules as we described in section III.F.

IV. CONCLUSIONS

In summary, we have tested the first wetting layer on the GaN (0001) surface with various adsorption models via DFT calculations and found that the dissociation of water adsorbates should obey the electron counting rule. The water adsorption on the GaN (0001) surface is not like one will predict to be 100% at the first glance of P.-T. Chen’s study. The maximum number of chemical bonds forming on the surface is 12, which implies the dissociation ratio of water on the GaN (0001) surface is 0.375 ML at low temperature and 0.75 ML coverage for hydroxyl group adsorption. Meanwhile, the evolution of density of states could be explained as well according to electron counting rule. On the other hand, the hydrogen bond strength between one water molecule at the upper layer and the first wetting layer is comparable to the energy difference between intact and dissociated water adsorbates. Hence, the consideration of the interaction from bulk water is needed to improve the understanding of water/catalyst interface in order to investigate water behavior near the surface as Tan did. With the success of using the electron counting rule in the explanations to our calculations, we suggest that the electron counting rule is a common rule applied to the water adsorption on polar III–V and II–VI semiconductor surfaces.

ASSOCIATED CONTENT

Supporting Information

Additional supporting figures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

This work is supported by Academia Sinica under Research Program on NanoScience and NanoTechnology, the National Science Council of Taiwan (NSC98-113-M-001-029-MY3 and NSC101-113-M-001-023-MY3), and the National Center for Theoretical Sciences (South) Physics Division. Computational resources in part are supported by the National Center for High Performance Computing.

REFERENCES


dx.doi.org/10.1021/jp313277i J. Phys. Chem. C 2013, 117, 8774–8873