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First-Principles Calculations of Hydrogen Generation Due to Water Splitting on Polar GaN Surfaces

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We present the chemical reactions leading to hydrogen gas generation via water splitting on polar GaN surfaces, which can be a significant source of renewable energy. To build an understanding at the atomic level of the activations afforded by the GaN (0001) and (000$\bar{1}$) surfaces, we determine the reaction mechanism of hydrogen generation on the polar faces using density functional theory calculations. The calculation results show that the first H splitting from water can occur with ground-state electronic structures; the barriers of H_2O splitting are 0.10 and 0.34 eV on the Ga-face and the N-face, respectively. However, the second H splitting requires huge energies of 1.42 and 1.73 eV, respectively, on the Ga-face and the N-face. Although the polar GaN surface can catalyze the first hydrogen splitting from water, we suggest that photoexcitation should be necessary for the second splitting.

1. Introduction

One of the main issues facing humans in the 21st century is the need to find a source of clean, low-cost, and environmentally friendly energy. Hydrogen gas (H_2) is one of the most significant sources of sustainable energy;[1,2] therefore, photogeneration of hydrogen from water attracts a lot of attention. Photocatalysis using semiconductors is widely studied.[3−14] The mechanism of water splitting on a semiconductor during photocatalysis involves semiconductors (band gap ∼2 eV) absorbing the ultraviolet light and most of the visible light of the solar spectrum and promoting electrons to excited states. An electron−hole pair is produced by the absorption of a photon. For a p-type semiconductor, electron transport at the water−semiconductor interface leads to reduction at the surface; see Figure 1. Therefore, the catalysis directly converts light to chemical energy (i.e., the reduced H_2).[3−6]

Among semiconductor materials, titanium dioxide (TiO_2) is an interesting potential semiconductor for photocatalysis,[5−8] and it has attracted much attention in recent decades following the pioneering work of Fujishima and Honda on TiO_2.[5] Despite its large band gap (3 eV in the rutile phase), TiO_2 has become a benchmark material for understanding the photooxidation process in the water-splitting reaction. The wide band gap of TiO_2 is not in the visible light region, which makes the efficiency of the photoenergy conversion lower. For this reason, some chemically modified TiO_2 have been synthesized to obtain an appropriate band gap.[7,8]
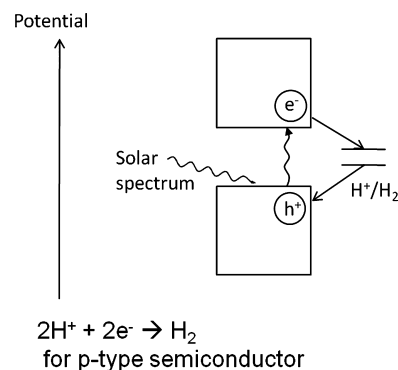

Figure 1. Diagram showing H_2 generation from water by a photoassisted semiconductor.

$$2H^+ + 2e^- \rightarrow H_2$$
for p-type semiconductor

Recently, the polar GaN surfaces have been proposed as being sufficiently accessible for water adsorption and splitting to occur.[9−14] The stability of GaN, coupled with its suitable band gap, makes it an interesting material to study for fundamental investigations of semiconductor electrochemistry and for applications, such as for use as an electrode. In addition to the optoelectronic applications, there is interest in the chemical activity, among various properties, of GaN surfaces. Photoelectrochemical reactions occur at the solid surface, and the surface structure and surface condition are expected to affect the reaction mechanisms.

However, there are few reports concerning H_2 generation at the water−semiconductor interface because splitting reactions are difficult to observe experimentally. First-principles theoretical calculations can help us to understand the chemical mechanism in such systems at the atomic level.[15] For GaN, even though some studies presented a good understanding of that surface activity causes H_2 and H_2O molecules to adsorb,[16,17] we still knew few characteristics of H_2 generation on the polar GaN surface. To answer the question of how H_2 is generated

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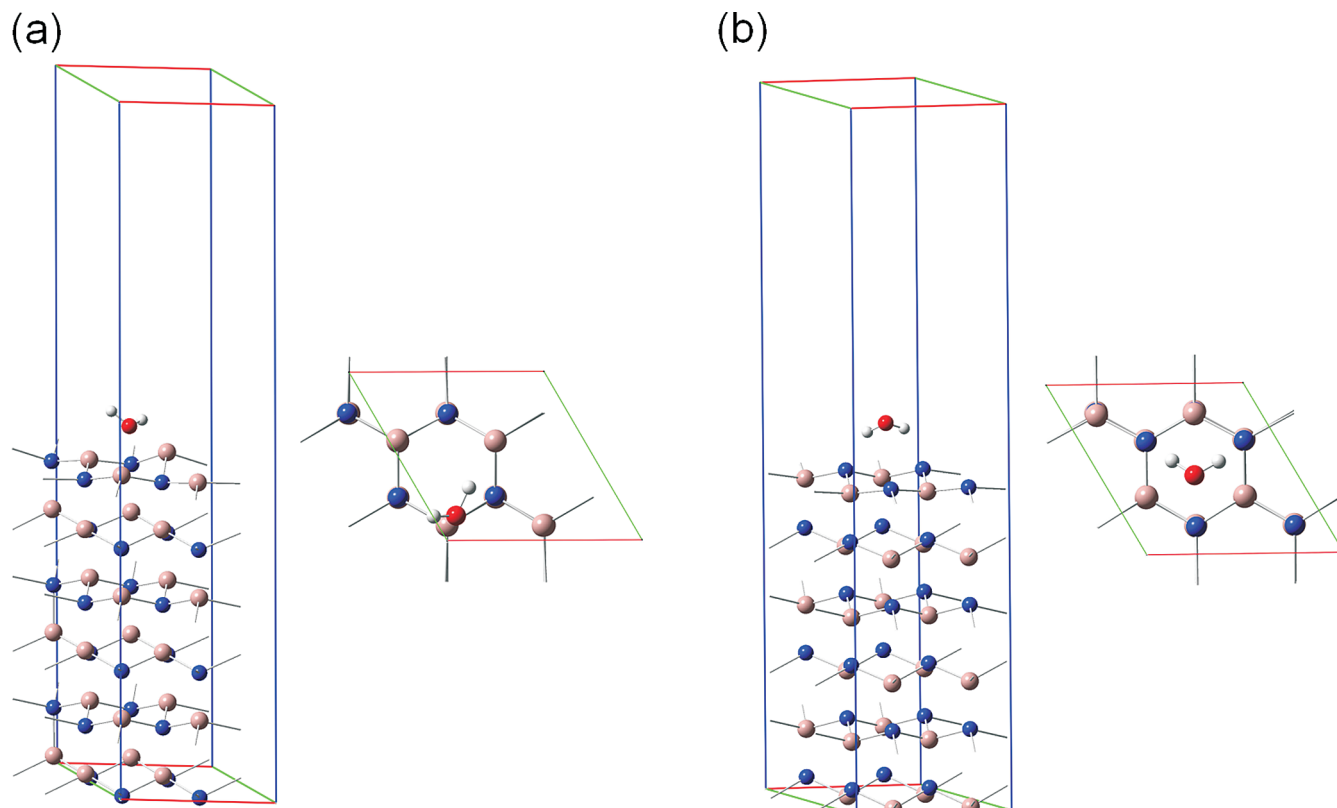§ National Central University.
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(a)

(b)

Figure 2. Supercells of a single H_2O molecule on the (a) Ga-face and the (b) N-face of GaN.

on a GaN surface, we performed density functional theory (DFT) calculations of the dissociation of a H atom from H_2O on a GaN (0001) and a (000$\bar{1}$) surface (Ga-face and N-face, respectively). Our results show that the Ga-face has a higher aptitude for H splitting than does the N-face. For the first H splitting, the polar GaN surfaces can catalyze the reaction in the ground state. However, the second H splitting on both surfaces has a huge energy barrier. We suggest that this paper will advance the further understanding of H_2 generation on p-type GaN surfaces.

2. Computation Method

Our calculations were performed with the Vienna Ab initio Simulation Package (VASP) code[18−20] with the generalized gradient approximation (GGA). The first-principles pseudopotential approach[21−23] Perdew-Wang91 was chosen as the exchange and correlation functionals, and the spin-polarization effect was considered. A spin-polarized calculation with an energy cutoff of 400 eV and a $5 \times 5 \times 1$ Monkhorst−Pack grid[24] was conducted. The GaN surfaces were modeled by a (2 $\times$ 2) supercell with six double-layers of slab and at least a 10 Å vacuum region, to focus the concern at the interface of single H_2O and GaN surfaces. We fixed one bottom double-layer to obtain better surface relaxation energies. The climbing nudged elastic band (cNEB)[25−28] method was used to determine the reaction processes of H dissociation. The cNEB method is a small modification to the NEB method in which the highest energy image is driven up to the saddle point; it will be at the exact saddle point.

3. Results and Discussion

A. Water Adsorbed on Polar GaN Surfaces. To characterize chemical reactions on GaN, we have optimized the H_2O molecule in various geometries on the polar GaN surfaces as a

first step (i.e., H_2O on 1-, 2-, or 3-fold sites). We found that H_2O on the top site of Ga on the Ga-face was the global minimum, which is showed in Figure 2a. The O atom has an interaction with Ga. One of the H−O bonds is almost parallel to surface, and the H atom that points to the nearest Ga atom is 2.31 Å from the nearest Ga atom. The other H−O bond dangles with the H atom pointing toward the vacuum. The adsorption energy of this structure of H_2O on the Ga-face is 1.68 eV; it can be considered as a strong electronic interaction. On the N-face, the global minimum is H_2O on the center of three N atoms, which is shown in Figure 2b. O has no obvious interaction with the surface. The two H−O bonds point toward two surface N atoms at distances of 2.03 and 2.98 Å, seemingly forming asymmetric hydrogen bonds. The adsorption energy of this structure of H_2O on the N-polar surface is 1.13 eV. Generally speaking, the structures of H_2O on the Ga-face have larger adsorption energies than do those on the N-face. We claim that the Ga-face has more electronic interaction with water and, therefore, can be more active in the water reaction.

B. Water-Splitting Reactions. Using these global minimum structures as reactants, we investigated a possible chemical reaction path. The splitting reaction and its potential energy surface on the Ga-face are shown in Figure 3. From the above discussion of the global minimum reactant, one can infer that the formation of an electronic interaction between the O atom and the Ga atom weakens the O−H bond, facilitating splitting. The first splitting of a H atom from water is an exothermic reaction, and the energy barrier of this reaction is a moderate 0.10 eV. Even at room temperature, this step can work if a small amount of energy is provided. This step can be considered a catalysis process; the Ga-face can facilitate H dissociation. It follows that the Ga-face might possibly be distributed with Ga−H species. During the second splitting reaction, the H atom of OH can approach and bond to a Ga−H species on the Ga-
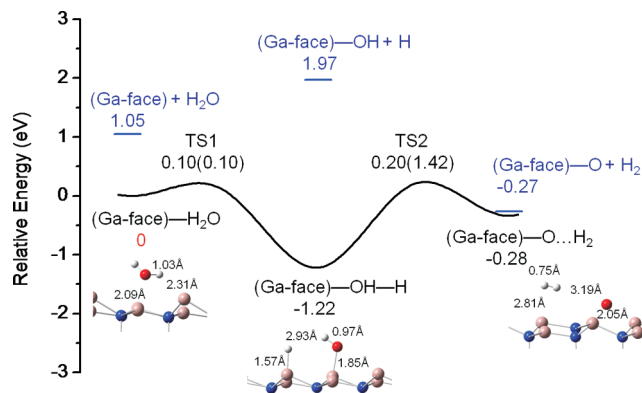
Figure 3. Geometries and relative energies obtained from theoretical calculations of water splitting on the Ga-face. The numbers are the relative energies in units of eV, and inside the parentheses are the energy barriers. The rate-determining step on the Ga-face has a barrier of 1.42 eV.
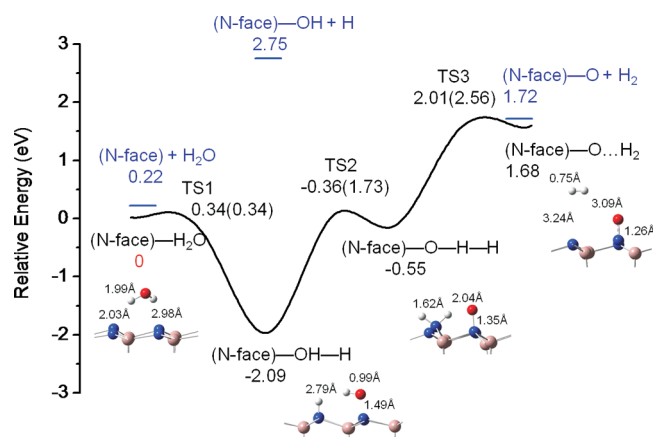

Figure 4. Geometries and relative energies obtained from theoretical calculations of water splitting on the N-face. The numbers are the relative energies in units of eV, and inside the parentheses are energy barriers. The rate-determining step on the N-face has a barrier of 2.56 eV.

face. H_2 can then form directly if the energy barrier of 1.42 eV is surmounted. The distance between the H_2 molecule and the Ga-face increases to 2.81 Å, at which point it can easily desorb from the Ga-face.

However, the second H splitting needs 1.42 eV to make the reaction occur; the reaction does not occur spontaneously at room temperature. Desorption of Ga–H requires 3.19 eV, which is a considerable amount of energy. Therefore, we suggest photoexcitation of an electron to a higher electronic state as a method to overcome the barrier. Globally, H_2 production is exothermic by 0.28 eV. The overall reaction is sufficiently efficient at energy conversion for this to be considered as a candidate for a new energy source.

The potential energy surface of the reaction pathway for the N-face is shown in Figure 4. Both H–O bonds of water interact with the N-face. The O atom is in the 3-fold center of three N atoms. The first H splitting yields an OH radical and simultaneously forms a N–OH bond. The energy barrier is moderate, 0.34 eV, which is larger than that on the Ga-face. The other H then splits. H_2 can be produced when two H atoms desorb from the N-face.

H_2 production on the N-face is endothermic, costing 1.68 eV. Notably, the reaction steps involving the second H splitting and N–H_2 dissociation have high barriers of 1.73 and 2.56 eV, respectively. If photoassistance was involved here, then the

photon should excite an electron by at least 3.77 eV (i.e., 1.68 − (−2.09) eV) to produce H_2. Only some UV light can participate in this step. Therefore, the N-face has less ability to photocatalyze water splitting than does the Ga-face.

The second H also can split from OH along GaN surfaces. The H atom then forms an X–H bond (where X = Ga or N). Therefore, the second H splitting leads to an intermediate state in which there are two disassociated X–H species on the surface. However, from Figure 5, we find that the energy barrier for two H atoms desorbing from the Ga-face and forming H_2 gas is 1.94 eV. The energy barrier for two H atoms desorbing from the N-face and forming H_2 gas is 5.32 eV. We do not prefer these reaction steps.

C. Proposed Electron Transfer between Water and the GaN Surface. An inexpensive method for correcting for the band gap has been the GGA + U method, and U = 10 eV on the Ga d states was adopted in this study.[29] On the basis of the method, the density of states (DOS) of the optimized structures that form after the first hydrogen splitting step on polar GaN surfaces have been calculated and are shown in Figure 6. Generally, the calculated band gap of the GaN surfaces was smaller than the experimental band gap of the bulk (~3.4 eV) because of the surfaces' relaxation, the adsorbate–surface interaction, and/or the just-sufficient +U value. However, our purpose was to provide theoretical characterizations of electron transfer rather than to pursue exact values. The experimental picture of electron transfer across the molecule–semiconductor interface was established.[30,31] When the GaN surface adsorbs a solar photon, an electron on the surface can be excited into unoccupied states; then electron transfer occurs between the interfaces and H_2O, which facilitates the H reduction. According to our above calculations, photoassistance is not necessarily involved in the first H splitting on either the Ga-face or the N-face because, even in the ground state, the reactions can be easily catalyzed.

Photoassistance can possibly occur after the first H splitting; the DOS are shown in Figure 6a-2,b-2. We can observe obvious electronic couplings between the GaN surfaces and H, which result in the GaN's band gap increasing. In this situation, the DOS of H1, which is broad and delocalized, can correspond with the DOS of GaN. The band gap of the Ga-face is about 2.2 eV, as is the main band gap of H; see Figure 6a-2. The photoexcited state is higher than the barrier of the second H splitting. H_2 can then be produced via changes in the internal electronic conversion.

Figure 6b-2 shows a band gap of the N-face, which is about 2.8 eV. The band gap is sufficiently large to overcome the second H splitting. However, from this structure, the H_2 production energy is at least 3.77 eV. This could imply that the electron might adsorb photons with higher energy and should be excited to higher electronic states or that the reaction might follow another path.

Although H_2 is produced on polar surfaces, the DOS of H_2 are localized. The main band of H_2 on the Ga-face is about −6 eV, and on the N-face it is about −4 eV. It means that the electron transfer across the GaN–H_2 interface does not occur easily. Therefore, we suggest that the photoassistance does not aid H_2 in desorbing from the polar GaN surface.

The DOS discussion in this paper is based on the GGA + U method in the electronic ground state. However, more appropriate methods for describing this system can be real-time, real-space excitation calculations, such as time-dependent density functional theory (TDDFT) and/or the GW/BSE method.[32] It is still difficult to practice calculations of photoinduced chemical
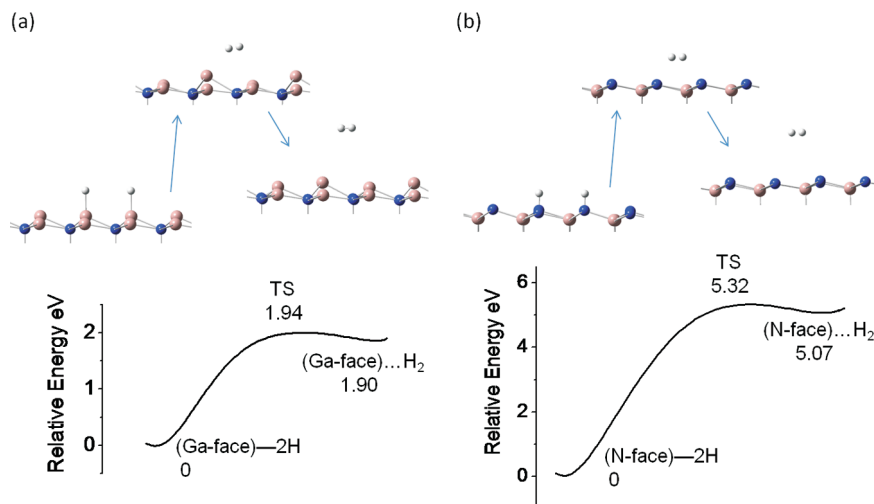
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Figure 5. Relative energy of the hydrogen migration reaction, $2H \rightarrow H_2$, on the (a) Ga-face and the (b) N-face. The hydrogen has an ability to form stronger bonds on the N-face than on the Ga-face. Therefore, the desorption of H from the N-face requires higher energy.
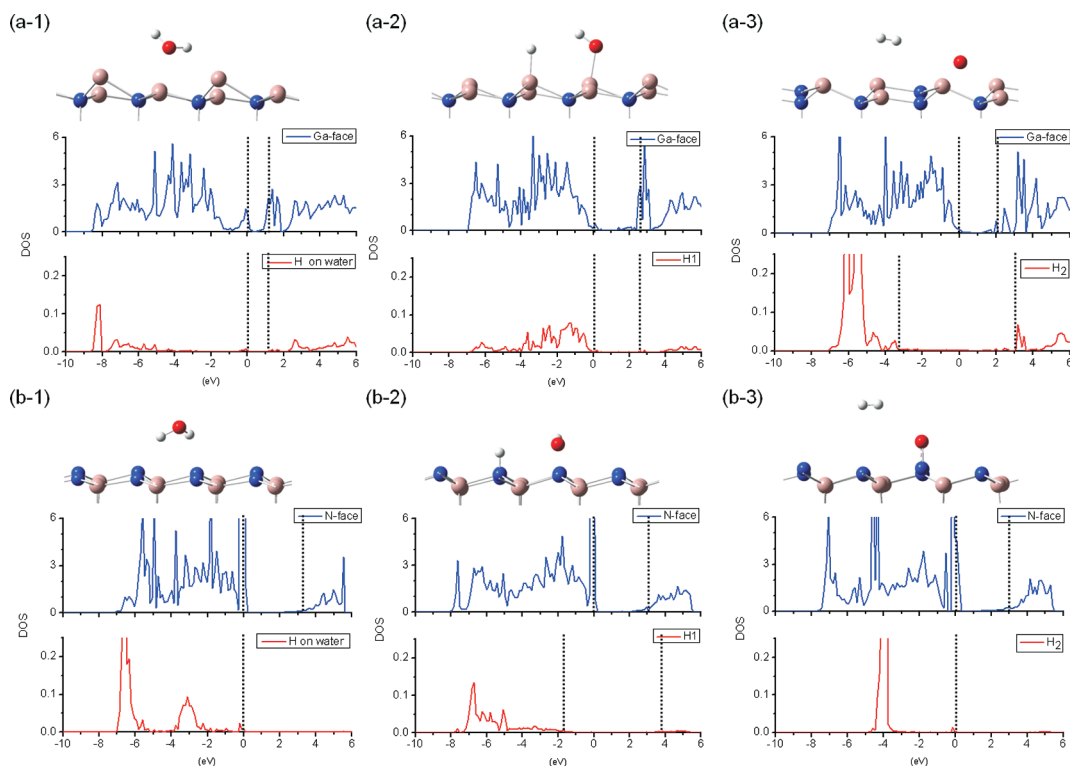

Figure 6. Density of states (DOS) of water splitting on the polar GaN surface, calculated by GGA + U. (a-1) H_2O, (a-2) one H splitting, and (a-3) two H splitting on the Ga-face. (b-1) H_2O, (b-2) one H splitting, and (b-3) two H splitting on the N-face.

reactions on such extended systems using these methods. Thus, our future research efforts will be focused on applying these excitation calculations to study a mechanism of photoinduced chemical reactions on GaN surface.

4. Conclusion

We have established a fundamental mechanism to understand how a single H_2O molecule interacts with polar GaN surfaces to generate H_2. For the Ga-face, two transition states (TSs) with the barrier energies of 0.10 and 1.42 eV have been identified. For the N-face, we have found three transition states with barrier energies of 0.34 eV (the first TS), 1.73 eV (the second TS), and 2.56 eV (the third TS). Our calculation results show that the first H splitting on both surfaces is catalyzed. Because the second step on the Ga-face and the last two steps on the N-face

require extra energies to overcome the barriers, visible−ultraviolet light absorption is one of the plausible means for this specific case. Although the real experimental conditions involve a more complex environment, the current work presents an ideal case. Adding further complexity will be a high priority in our future research.

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