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# Cooperative Roles of Chemical Reactions and Mechanical Friction in Chemical Mechanical Polishing of Gallium Nitride Assisted by OH Radicals: Tight-Binding Quantum Chemical Molecular Dynamics Simulations

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**Abstract**

Chemical mechanical polishing (CMP) is a key manufacturing process for applying gallium nitride (GaN), especially the Ga-face GaN, to semiconductor devices such as laser diodes. However, the CMP efficiency for GaN is very low due to its high hardness and chemical stability. Experimentally, OH radicals appear able to improve the CMP efficiency of GaN polished by a SiO<sub>2</sub> abrasive grain, whereas the mechanisms of the OH-radical-assisted CMP process remain unclear because experimental elucidation of the complex chemical reactions occurring among GaN substrate, abrasive grain, and OH radicals is difficult. In this work, we used our previously developed tight-binding quantum chemical molecular dynamics simulator to study the OH-radical-assisted CMP process of the widely employed Ga-face GaN substrate polished by an amorphous SiO<sub>2</sub> abrasive grain in an effort to understand how OH radicals assist the CMP process and then aid the development of next-generation CMP techniques. Our simulations revealed that the OH-radical-assisted CMP process of GaN occurs via the following three basic reaction steps: (i) first, all hydrogen terminations on the GaN surface are replaced by OH terminations through continuous reactions with OH radicals; (ii) after the substrate is fully terminated by OH, the hydrogen atoms of these OH terminations are removed by reacting with newly added OH radicals, which forms H<sub>2</sub>O molecules and leaves energetic oxygen atoms with dangling bonds on the surface; and (iii) finally, these energetic oxygen atoms intrude inside the substrate with concomitant dissociation of Ga–N bonds and the generation of N<sub>2</sub> and gallium hydroxide molecules, which accumulatively lead to the removal of N and Ga atoms from the substrate.

**Keywords:** molecular dynamics simulation, CMP, gallium nitride, hydroxyl radical

## 1. Introduction

Gallium nitride (GaN) is a promising material for blue and ultraviolet laser diodes (LDs) because of its wide band gap and high saturation electron speed compared with silicon.<sup>1,2</sup> GaN is also used in field-effect transistors (FETs) that are expected to be used in next-generation electronic devices with high voltage, high frequency, and low power consumption.<sup>3</sup> In the manufacture of high-power LDs and high-efficiency FETs, defect-free epitaxial GaN films are typically grown on atomically smooth GaN substrates. Thus, the production of atomic-level planar GaN substrates is crucial. Chemical mechanical polishing (CMP) has been used for atomic-level planarization of a diverse variety of materials, such as silicon, sapphire, copper, and glass.<sup>4-7</sup> In the general CMP process, assisted by the mechanical friction with abrasive grains, the to-be-polished substrate is first oxidized by the oxidative slurry (e.g.,  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$  solvent) and then the oxidized surface is mechanically polished. However, although CMP is effective for materials such as silicon and sapphire, it is difficult to polish GaN efficiently by CMP because of its high hardness and chemical stability. For example, Aida *et al.* reported a material removal rate (MRR) of 17 nm/h during the polishing of a GaN(0001) substrate using  $\text{SiO}_2$  as the abrasive grain and an alkaline solvent (pH 10.5), which is over 100 times slower than that for the CMP of silicon substrates.<sup>8</sup>

Recently, some studies have employed the Fenton reaction<sup>9</sup> to improve the CMP efficiency for GaN. The Fenton reaction involves the generation of OH radicals by a catalytic reaction between Fe and  $\text{H}_2\text{O}_2$ . By exploiting the OH radicals generated, Murata *et al.* reported an MRR of 32 nm/h,<sup>10</sup> while Zou *et al.* achieved an MRR of 66.88 nm/h and a surface roughness of 0.056 nm using  $\text{SiO}_2$  as the abrasive grain.<sup>11</sup> The MRR of GaN polished using  $\text{SiO}_2$  abrasive grain was even reported to reach 77.05 nm/h when a Pt/C

catalyst was used to accelerate the generation of OH radicals.<sup>12</sup> These studies demonstrate that OH radicals can greatly improve the CMP efficiency for GaN. Therefore, understanding the mechanisms underlying the OH-radical-assisted CMP processes is crucial for further improving and optimizing the CMP techniques for higher efficiency. However, the chemical reactions between the GaN substrate, OH radicals, solvent, and abrasive grain are very complex, so that it is difficult to gain insights into the atomic-scale CMP mechanisms experimentally.

Computational simulation is a useful tool for revealing the intricate chemical reactions and mechanisms involved in CMP processes. Classical molecular dynamics (MD) methods have been used to investigate CMP processes in which chemical reactions need not be considered, such as material damage and deformation, chip formation, and thermal effects.<sup>13–18</sup> However, the classical MD approach cannot adequately deal with processes in which chemical reactions play a significant role. In contrast to classical MD, quantum chemical methods are suitable for faithfully describing chemical reactions. For example, Chen and Kuo used static first-principles calculations to examine the interfacial interactions between GaN (0001) substrate and water.<sup>19</sup> Oue *et al.* investigated the hydrolysis process at the kinked and stepped sites of GaN surface by using density functional theory (DFT), which revealed that the dissociation of water was more strongly favored at the kinked sites than at the stepped sites.<sup>20</sup> Furthermore, besides static analysis, first-principles MD is a promising method for accurately studying the reaction dynamics. However, first-principles MD is not suitable for prolonged simulations or large-scale systems owing to its huge computational cost, and consequently this approach has not yet been applied to CMP simulations to the best of our knowledge. Thus, there exists a strong demand for the development of much faster quantum chemical MD methods to simulate

the reaction dynamics during CMP processes. In our previous research, we have developed a tight-binding quantum chemical molecular dynamics (TB-QCMD) code that is applicable to larger systems and longer calculations than first-principles MD.<sup>21–24</sup> We have successfully applied this TB-QCMD code to a variety of systems, such as plasma etching, plasma-enhanced chemical vapor deposition, and tribochemical reactions.<sup>25–31</sup> Furthermore, we have also used the TB-QCMD code to examine the CMP process of copper.<sup>32,33</sup> In our previous paper,<sup>33</sup> we simulated the CMP of a copper substrate using a SiO<sub>2</sub> abrasive grain in aqueous H<sub>2</sub>O<sub>2</sub> solution and successfully revealed the chemical reaction dynamics induced by mechanical friction between the substrate and abrasive grain. However, studies on the CMP process of GaN are still lacking. In this work, we applied our previously developed TB-QCMD simulator to the OH-radical-assisted CMP process of GaN(0001) in order to elucidate how OH radicals benefit the rapid polishing of GaN in experiments<sup>10–12</sup>, with the aim of contributing to the development of next-generation CMP techniques.

Specifically, to simulate the continuous reaction between OH radicals and the GaN substrate, we first incorporated an algorithm into our CMP simulator that allows for the continuous addition of OH radicals into the simulation system. Next, we performed CMP simulations for a GaN(0001) substrate polished by an amorphous SiO<sub>2</sub> in aqueous solution with and without OH radicals, to reveal the effect of OH radicals on the CMP process. Finally, to confirm the validity of the reactions between OH radicals and GaN observed in the TB-QCMD simulations, we conducted static DFT calculations to verify the above findings from an energetic perspective. Our results reveal the detailed cooperative roles of chemical reactions and mechanical friction by SiO<sub>2</sub> abrasive grains in the CMP process of GaN substrate.

## 2. Tight-Binding Quantum Chemical Molecular Dynamics Method

Our developed TB-QCMD simulator is able to simulate the complicated chemical reactions that occur during CMP processes. In our previous work,<sup>33</sup> we used the TB-QCMD simulator to model the CMP process at a three-phase interface between the abrasive grain, substrate, and aqueous chemical solution. However, simulations of continuous CMP processes are difficult because the reactants in aqueous solution are gradually consumed by the chemical reactions, which causes the reactions to cease due to the absence of reactants. In this work, to study the continuous chemical reactions with OH radicals during the CMP process, we extended our TB-QCMD-based CMP simulator by introducing a new algorithm that continuously adds OH radicals into the CMP system during the simulation. Next, we used this modified simulator to examine the CMP process of a GaN substrate using SiO<sub>2</sub> abrasive grain in aqueous solution with the continuous addition of OH radicals. The used TB-QCMD parameters were reported in our previous work.<sup>34</sup>

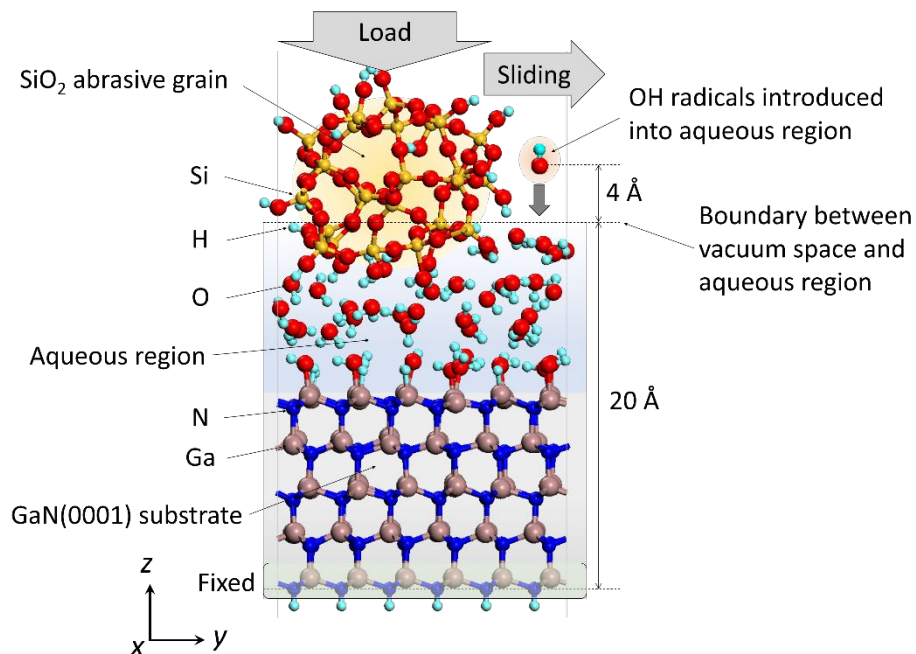
Figure 1 shows the CMP simulation model of a GaN(0001) substrate with a SiO<sub>2</sub> abrasive grain in aqueous solution. The surface of GaN(0001) substrate is capped by Ga atoms. As fully reviewed previously<sup>35</sup>, this Ga-face GaN is more stable than N-face and moreover Ga-face has higher 2-dimensional electron density than N-face, which makes Ga-face GaN more suitable for using in power integrated circuits and piezoelectric devices. This huge application potential of Ga-face GaN is the reason why the above referred GaN CMP experiments<sup>10–12</sup> paid attention to the Ga-faced GaN(0001). While, SiO<sub>2</sub> is one of the most widely used abrasive grain in experiments because it could realize the both high material removal rate and ultra-smooth surface with less scratches. The SiO<sub>2</sub> surface is fully terminated by hydroxyl groups, because the slurry used in the above OH-

radical-assisted CMP experiments<sup>10–12</sup> shows slight acidic and hence there are no deprotonation reactions of the surface hydroxyl groups<sup>36</sup>. Periodic boundary conditions were employed in the  $x$ ,  $y$ , and  $z$  directions with dimensions of 9.68, 16.77, and 50.00 Å, respectively. A GaN(0001)-(3×6) slab consisting of 90 Ga atoms and 90 N atoms was used as the substrate model. Here, the topmost GaN(0001) surface is covered by Ga atoms and the bottommost GaN(0001) surface is covered by N atoms. The lowest bilayer of the slab was fixed and the bottommost N layer was fully terminated by hydrogen atoms. The free upper surface of the substrate was passivated by fully relaxing in pure water, which results in the formation of hydrogen and hydroxyl terminations on the surface. For the SiO<sub>2</sub> abrasive grain, a fully OH-terminated amorphous SiO<sub>2</sub> cluster was placed above the GaN substrate. The region between the GaN substrate surface and a distance of 20 Å from the fixed nitrogen layer was uniformly filled with H<sub>2</sub>O molecules (aqueous region in Figure 1). To perform the CMP simulations, the upper SiO<sub>2</sub> layer (11 Si atoms) was subjected to a normal load of 1.6 nN and forcibly slid along the  $y$  direction at a velocity of 50 m/s. Since the presently used SiO<sub>2</sub> abrasive grain is much smaller than that the experimentally used ones, fixing the upper layer of SiO<sub>2</sub> will surely affect its mechanical properties more or less; however, there will be few influences on the present simulation and conclusions because the present work focus on only the chemical reactions at the SiO<sub>2</sub>/GaN interface rather than the deformation of SiO<sub>2</sub> abrasive grain. Prior to the CMP simulations, the SiO<sub>2</sub> abrasive grain was brought into contact with the substrate in water by the applied normal load until the position of the grain had stabilized. During this pressing process, some of the H<sub>2</sub>O molecules were expelled from the aqueous region, and then these out-of-region water molecules were removed from the simulation cell to keep the thickness of the aqueous region constant. Then, during the CMP simulation, OH



radicals were added into the aqueous region one by one to simulate the continuous chemical reactions. The to-be-added OH radical is firstly placed 4 Å above the aqueous region and then it is forcibly moved downward until completely entering the aqueous region. The external force would disappear when the OH radical goes across the vacuum/liquid boundary. The distance between the vacuum/liquid boundary and the GaN surface is about 10 Å which is far enough to avoid the effect of the external force on the chemical reactions between OH radicals and GaN surface. The first OH radical was added to the aqueous region after 10.0 ps of simulation; thereafter, the new OH radical was added after the previously introduced OH radical had reacted with the GaN substrate, ensuring a low concentration of OH radicals in the aqueous solution. Different to the real CMP slurry in experiments, there are no other chemical components (e.g. corrosion inhibitor and pH adjustor in the real CMP slurry) except the aqueous water and OH radicals in the present simulation model, because the major purpose of this article is just to fully understand the CMP mechanisms of GaN assisted by the oxidizer of OH radicals. Meanwhile, during the CMP process, the H<sub>2</sub>O molecules and added OH radicals were restricted within the aqueous region to prevent their diffusion into the upper vacuum area. If a H<sub>2</sub>O molecule or OH radical move out from the aqueous region, a downward force would be applied to this out-of-region molecule/radical until it enters the aqueous region again. In our simulations, the Verlet algorithm was used to evolve the atomic motion with a time step of 0.2 fs/step.<sup>37</sup> The temperature was controlled by scaling the atom velocities to maintain a temperature of 300 K. This velocity scaling thermostat has been proved in many previous papers to be effective for various atomic-scale problems including the friction<sup>38,39</sup>, CMP<sup>33,34,40</sup>, materials' structures<sup>41</sup>, and etching processes<sup>25</sup>. To examine the effect of OH radicals on the CMP mechanism and efficiency, CMP simulations of GaN

with and without OH radicals were performed and compared.



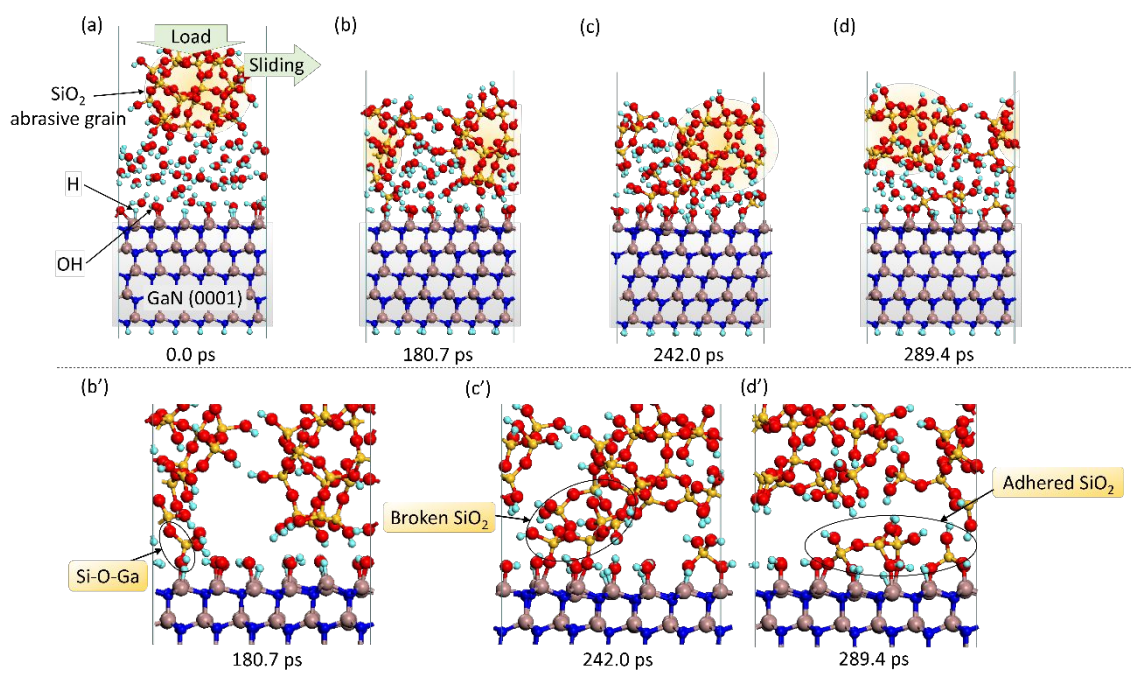
**Figure 1.** CMP simulation model of a GaN(0001) substrate with a SiO<sub>2</sub> abrasive grain in aqueous solution with continuous addition of OH radicals.

### 3. Results and Discussion

#### 3.1 CMP Simulation in Pure Water

We first performed a CMP simulation of the GaN(0001) substrate with the SiO<sub>2</sub> abrasive grain in pure water without OH radicals. Figure 2a–d show the snapshots of this CMP simulation. For a clearer depiction of the chemical reaction dynamics, Figure 2b'–d' show the magnified snapshots of the sliding interface, where H<sub>2</sub>O molecules are omitted for clarity. At 180.7 ps, the SiO<sub>2</sub> abrasive grain first reacted with the GaN by forming a Si–O–Ga bond at the sliding interface (Figure 2b and 2b'). Then, the SiO<sub>2</sub> abrasive grain and GaN substrate are dragged with each other via the formed Si–O–Ga bond. Because the Ga atom of the Si–O–Ga bond is tightly constrained in its original

position, the stretching of this Si–O–Ga bond during continued sliding results in the dissociation of some Si–O bonds in the abrasive grain (Figure 2c and 2c' at 242.0 ps). With the further cleavage of Si–O bonds during sliding, at 289.4 ps some of the O and Si atoms in the SiO<sub>2</sub> cluster became detached from the abrasive grain and were finally transferred to the GaN substrate (Figure 2d and 2d'). After the overall 400.0 ps of simulation, we confirm that the GaN substrate is not polished by the SiO<sub>2</sub> abrasive grain in the pure water system without OH radicals. This result is not surprising, as previous experiments<sup>8,42</sup> also indicated that it is difficult for SiO<sub>2</sub> abrasive grain to polish GaN substrates in the absence of active species such as OH radicals. For example, Tavernier *et al.* reported that there was no significant change in the surface morphology of GaN after polishing with SiO<sub>2</sub> abrasive grain without active species.<sup>42</sup> Thus, our simulation results are in qualitative agreement with these experimental results of GaN.



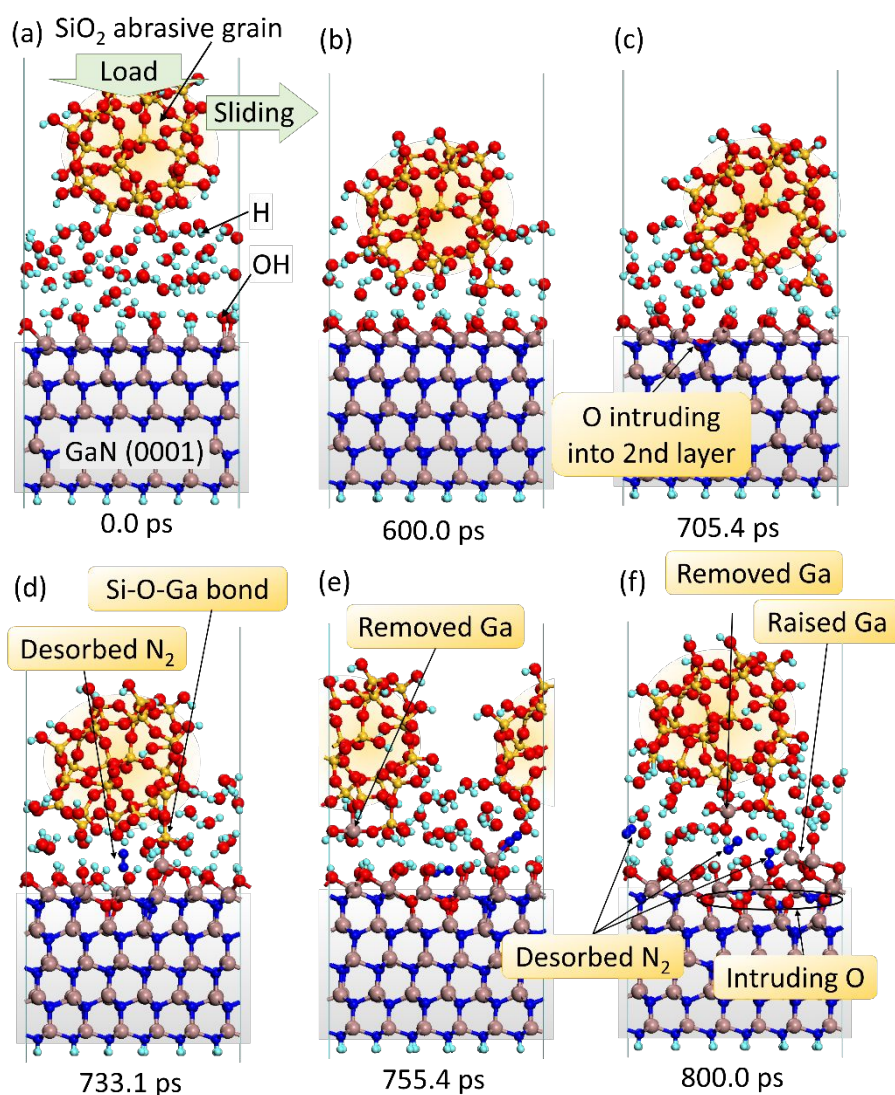
**Figure 2.** Snapshots of the CMP simulation of the GaN(0001) substrate with the SiO<sub>2</sub> abrasive grain in pure water after (a) 0.0, (b) 180.7, (c) 242.0, and (d) 289.4 ps. The position of the SiO<sub>2</sub> abrasive grain is indicated by the translucent orange color. For a clearer depiction of the processes occurring at the interface, the lower part of the graphic shows magnified snapshots at (b') 180.7 ps, (c') 242.0 ps, and (d') 289.4 ps, where the water molecules are omitted for clarity.

### 3.2 CMP Simulation with OH Radicals

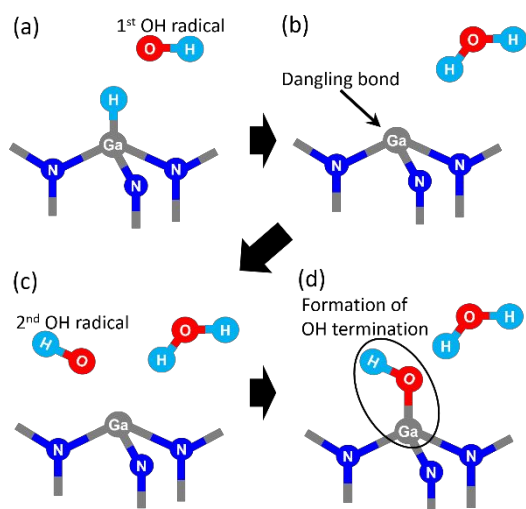
To examine the effect of OH radicals on the CMP process, we next performed a CMP simulation of the GaN(0001) substrate with the SiO<sub>2</sub> abrasive grain in the presence of OH radicals. To simulate the continuous chemical reactions, OH radicals were continuously added into the aqueous region. Figure 3 shows snapshots of the CMP process up to 800.0 ps. During the initial approximately 600.0 ps, the hydrogen terminations on the GaN surface were gradually replaced by OH terminations due to the reactions between the terminal H atoms and added OH radicals. Figure 4 shows a schematic depiction of the detailed reaction dynamics. When an OH radical approaches the surface (Figure 4a), it reacts with the terminal H atom to form a H<sub>2</sub>O molecule. This reaction leaves a dangling bond on the GaN surface (Figure 4b; next, the second OH radical comes and reacts with the dangling bond (Figure 4c) to form an OH termination (Figure 4d). Once the surface is fully terminated by OH groups, it is interesting to note that the subsequently added OH radicals continue to react with the OH-terminated GaN substrate. To highlight the detailed chemical reaction dynamics between the OH-terminated GaN substrate and OH radicals, Figure 5 presents magnified snapshots at the CMP interface between 693.7 and 733.1 ps. At 693.7 ps, the added OH radical in the aqueous region approached one of the OH

terminations on the GaN substrate (Figure 5a). The H atom in the OH termination was then taken away by the OH radical to generate a H<sub>2</sub>O molecule (Figure 5b). The residual terminal O atom on the GaN surface was unstable because it has a dangling bond, so that at 705.4 ps the unstable O atom intruded into the second layer of the GaN substrate with the aid of mechanical friction by the SiO<sub>2</sub> abrasive grain (Figure 5c). This process is the initial step in the oxidation of the GaN substrate. The above results reveal that the oxidation of GaN is caused by the collaboration of both chemical reactions (generating energetic terminal O atoms on the surface via several chemical reaction steps with OH radicals) and mechanical friction of abrasive grain (aiding the terminal O atoms intrude into the substrate), rather than solely by the attack of OH radicals. Furthermore, during the oxygen intrusion, the intruding oxygen atom pushes a nitrogen atom (which is in the second layer of the GaN substrate) toward its neighboring nitrogen atom, which interestingly results in the dissociation of Ga–N bonds and the formation of a new N–N bond (Figure 5c). Figure 6 shows a schematic illustration of this process, where Ga1, Ga2, and Ga3 denote atoms located in the topmost layer and Ga4 denotes an atom in the subsurface layer. Initially, the surface atom Ga1 has an energetic terminal O atom (O1) after the reaction with OH radicals. Then, the O1 atom intrudes inside the GaN substrate due to the mechanical friction by the abrasive grain. During this intrusion step, O1 occupies the original position of the N1 atom, causing the N1 atom to be pushed toward its neighboring N2 atom with concomitant dissociation of the Ga1–N1 bond and formation of a new N1–N2 bond. Furthermore, with the intrusion of the O atom and the formation of the N–N bond, the generated Ga–N–N–Ga structure in the substrate is highly distorted and tends to relax. As a result of the relaxation of the distorted Ga–N–N–Ga structure at 713.7 ps, a Ga atom is raised up from the surface at 730.9 ps (Figure 5d and

5e), and Figure 6c clearly shows the relationship between the relaxation of the Ga–N–N–Ga structure and the protrusion of the Ga atom. During the subsequent CMP process at 733.1 ps, this raised Ga atom collided with the SiO<sub>2</sub> abrasive grain to form a Si–O–Ga interfacial bond at the SiO<sub>2</sub>/GaN interface (Figure 3d and 5f). Subsequently, activated by the mechanically stretching of the Si–O–Ga bond, hydrolysis reactions between the raised Ga atom and surrounding H<sub>2</sub>O molecules take place, resulting in the breakings of the bonds between this raised Ga atom and its neighboring atoms as well as the generation of a hydrate molecule of gallium hydroxide (Ga(OH)<sub>3</sub>·H<sub>2</sub>O in Figure 3e). Then, the raised Ga atom is ultimately removed from the GaN substrate. As the CMP process proceeded with the continuous addition and reaction of OH radicals, one another oxygen atom intruded into the substrate again (Figure 5f), leading to further dissociation of Ga–N bonds. As a result of continuous dissociation of Ga–N bonds, a N<sub>2</sub> molecule is generated and evaporated from the GaN substrate surface (Figure 5f). These results indicate that the N atoms of the GaN substrate are removed from the surface through the desorption of gaseous N<sub>2</sub> molecules generated during the CMP process. By the end of the CMP simulation (800.0 ps), three N<sub>2</sub> molecules were desorbed from the GaN substrate, three Ga atoms were raised up, and one of the raised Ga atoms was removed from the substrate by the SiO<sub>2</sub> abrasive grain (Figure 3f). Overall, we successfully reveal that, assisted with the oxidation of GaN substrate by OH radicals, Ga and N atoms are removed from the GaN substrate via the generation of gallium hydroxide molecule (Ga(OH)<sub>3</sub>·H<sub>2</sub>O) and evaporation of N<sub>2</sub> molecules, respectively.



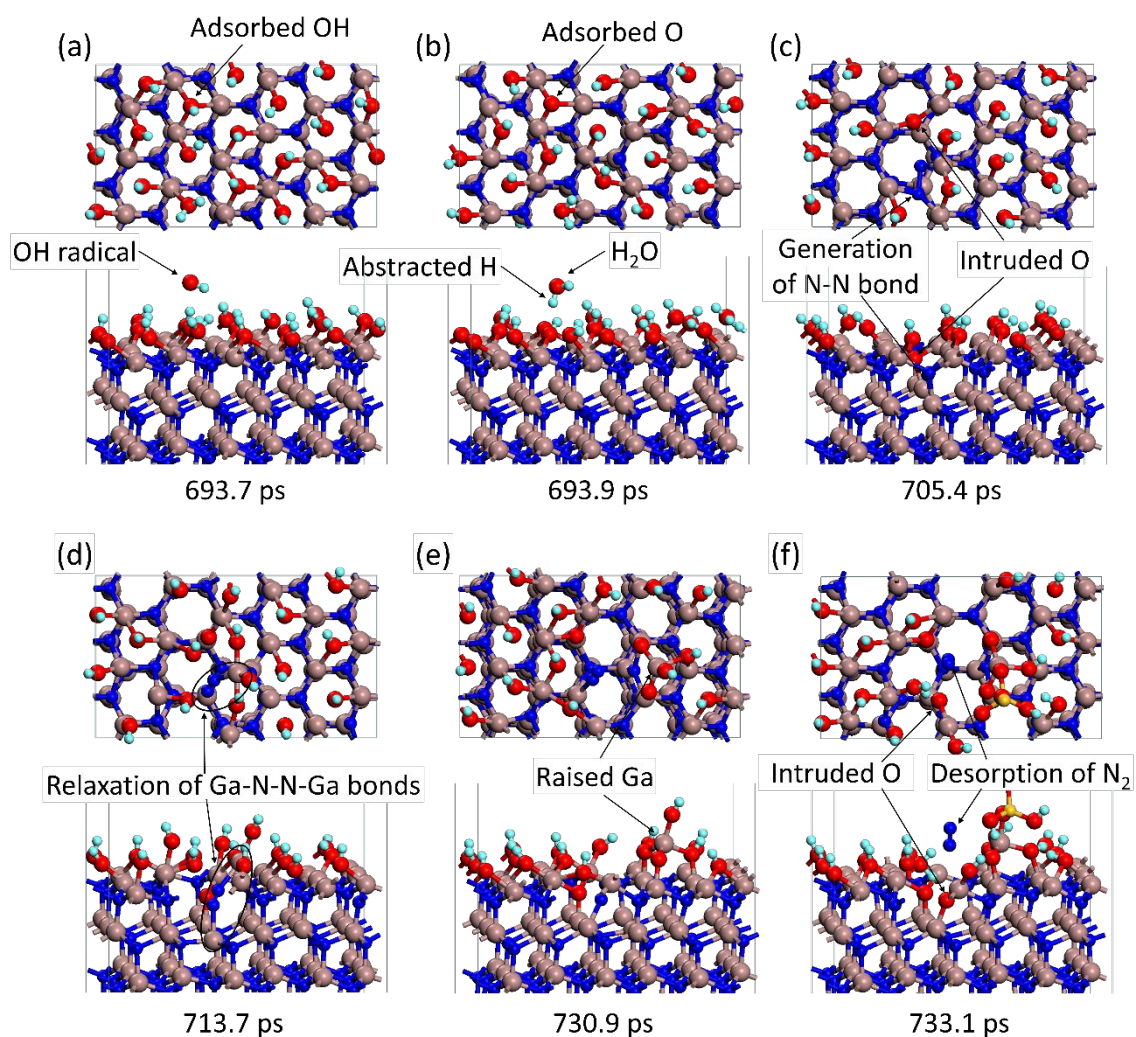
**Figure 3.** Snapshots of the CMP simulation of the GaN(0001) substrate with the SiO<sub>2</sub> abrasive grain in water with the continuous addition of OH radicals at (a) 0.0, (b) 600.0, (c) 705.4, (d) 733.1, (e) 755.4, and (f) 800.0 ps.



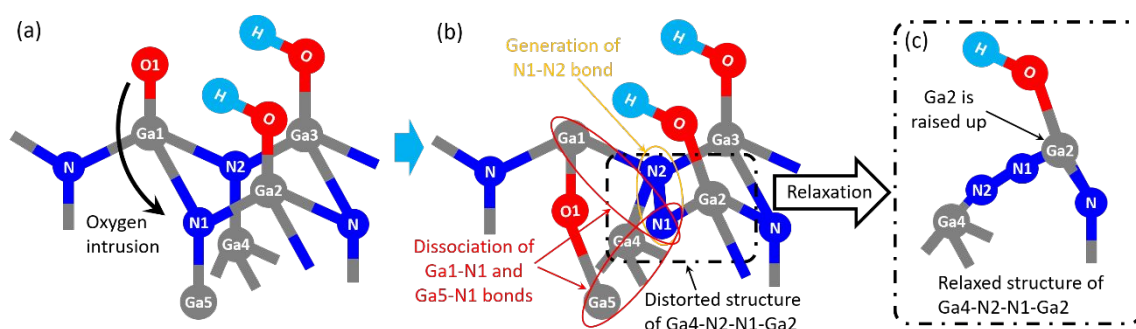
**Figure 4.** Schematic illustration of the reactions between OH radicals and GaN surface.

(a) The first OH radical approaches the H-terminated GaN surface and reacts with the terminal H atom to form (b) a H<sub>2</sub>O molecule and a dangling bond on the GaN surface. (c) A second OH radical then approaches and reacts with the dangling bond to form (d) an OH termination on the surface.





**Figure 5.** Snapshots of typical reactions between the OH-terminated GaN substrate and OH radicals at (a) 693.7, (b) 693.9, (c) 705.4, (d) 713.7, (e) 730.9, and (f) 733.1 ps. The upper and lower panels show the top and side views, respectively, of the GaN substrate.

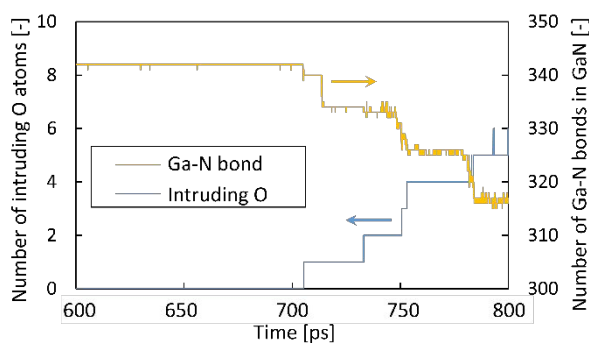


**Figure 6.** Schematic illustration of the oxygen intrusion process. (a) GaN surface with an energetic terminal O atom (O1). (b) Due to the intrusion of the O1 atom, the N1 atom is pushed away from its original position toward its neighboring N2 atom, which is accompanied by dissociation of Ga1–N1 and Ga5–N1 bonds and formation of a new N1–N2 bond. (c) Expanded view of the relaxed Ga2–N1–N2–Ga4 structure.

To quantitatively understand the effect of oxidation on the polishing of the GaN substrate, we counted the numbers of intruded oxygen atoms and Ga–N bonds in the GaN substrate during the CMP simulation, as shown in Figure 7. During the first 700.0 ps of the CMP process, the reactions with OH radicals only induce the generation of OH terminations (Figure 4), so that there were no intruded oxygen atoms and the number of Ga–N bonds remained unchanged. However, after the surface was fully terminated by OH groups at 705.4 ps, the first oxygen intrusion event occurred along with the dissociation of Ga–N bonds. Subsequently, the number of intruded oxygen atoms increased while the number of Ga–N bonds decreased. These results quantitatively demonstrate the strong correlation between the oxygen intrusion and Ga–N bond dissociation, which indicates that these two processes occur simultaneously. Thus, we suggest that oxidation of the GaN substrate is a key process for CMP because the oxidation-induced Ga–N bond dissociation is the origin of the subsequent removal of N

and Ga atoms.

In summary, the above simulation results reveal that the OH-radical-assisted CMP process of GaN proceeds via three key reaction steps: (i) first, OH terminations are generated on the GaN surface by chemical reactions between the terminal H atoms and OH radicals (Figure 4); (ii) additional OH radicals then further react with the H atoms of the OH terminations to form H<sub>2</sub>O molecules and terminal O atoms with dangling bonds (Figure 5a and 5b); and (iii) the terminal O atoms intrude into the GaN substrate surface with the concomitant dissociation of Ga–N bonds and generation of N<sub>2</sub> molecules (Figure 5c–5f).



**Figure 7.** Numbers of intruded oxygen atoms and Ga–N bonds in the GaN substrate during the CMP process with the continuous addition of OH radicals.

### 3.3 Confirmation of Chemical Reactions between GaN and OH Radicals by DFT Calculations

We also performed DFT calculations to further elucidate the mechanisms of the chemical reactions between OH radicals and the GaN substrate and verify the TB-QCMD simulation results. According to the above results, the key step in the radical-assisted CMP process is oxidation of the fully OH-terminated GaN substrate via reaction with OH

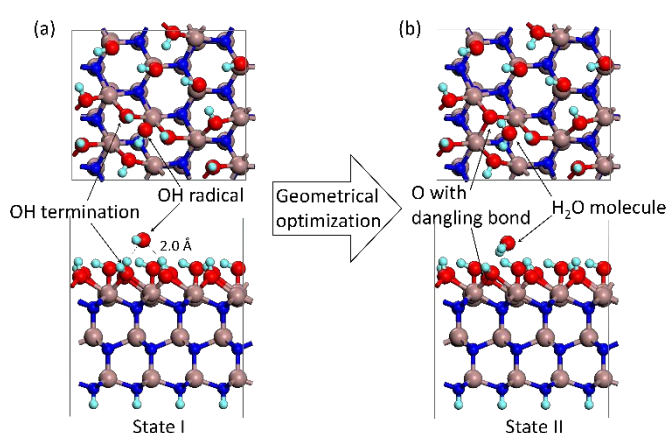
radicals. During this reaction, the OH radical must first take the H atom of the OH termination away from the surface by forming a H<sub>2</sub>O molecule, and then the residual terminal O atom with a dangling bond intrudes into the substrate. Therefore, the energetics of the above reactions were investigated by static DFT calculations. In this work, DFT calculations were performed using DMol<sup>3</sup> code<sup>43</sup> with the spin-unrestricted GGA-type PW91 functional and double numerical plus polarization basis set. An effective core potential method and global-space cutoff of 4.6 Å were employed.

As it is difficult to perform DFT calculations for systems as large as the one in the TB-QCMD simulations due to the huge computational costs, a small GaN(0001) substrate model was employed. Periodic boundary condition is applied to the cell with a size of  $9.675 \times 11.172 \times 40.000 \text{ \AA}^3$ . To make sure the model's surface structure used in DFT calculations as same as that used in the TB-QCMD simulations, this small GaN substrate was constructed via the following procedures: (i) initially a GaN substrate with a fully H-terminated lower surface and a fully OH-terminated upper surface was relaxed at 300 K by the TB-QCMD simulation, (ii) we picked up some structures at different MD steps and calculated their energies by DFT, and (iii) the structure with the lowest energy was adopted. To first study the reaction between the OH radical and OH termination, an OH radical was placed on an OH termination of the above constructed GaN model with a distance of 2.0 Å, as depicted in Figure 8a (state I), and then geometrical optimization of the state I model was performed using DFT. Figure 8b shows the optimized structure (state II), where the OH radical had reacted with its nearest OH termination on the GaN surface to generate a H<sub>2</sub>O molecule and a dangling bond on the surface. This indicates that the reaction between an OH radical and OH termination generates a H<sub>2</sub>O molecule and a terminal O atom with no activation barrier. This result agrees with the TB-QCMD

results shown in Figure 5a and 5b. Moreover, in the DFT calculations, the total energy of the optimized structure (state II) is lower than that of the initial structure (state I), indicating an exothermic reaction with a reaction energy of -16.7 kcal/mol. To confirm whether the TB-QC method could give the same results with the DFT calculations or not, the reaction energy is also checked by the TB-QC method. In details, the initial structure (state I) for the TB-QC method is same as that for the DFT calculation. The state II is relaxed by the TB-QC method to reach a stabilized structure, and hence we obtain the reaction energy of -10.1 kcal/mol which is the energy difference from the state I to II, indicating an exothermic reaction too, and the reaction energy reasonably agrees with that by the DFT calculations. It should be noted that the above reaction between OH radical and the OH termination of GaN substrate will spontaneously occur once a OH radical occasionally approaches the GaN surface and occurrence of this reaction is not influenced by the initial position of OH radical, as shown in the Figure S1 of the Supporting Information.

Next, the reactions of oxygen intrusion accompanied by Ga–N bond dissociation and N–N bond generation were examined using the post-reaction GaN substrate obtained above (state II) as the reactant. To afford the oxidized GaN substrate as the reaction product, the O atom with a dangling bond was manually inserted into the GaN substrate, and then geometrical optimization was performed using DFT. The optimized structure (state III) is depicted in Figure 9. After the optimization, in accordance with the TB-QCMD simulation results, the intruded O atom was stabilized in the GaN substrate while a Ga–N bond was dissociated and a N–N bond was formed. The total system energy of state III is lower than that of state II, indicating an exothermic reaction with a reaction energy of -21.9 kcal/mol. Additionally, in order to confirm the accuracy of the TB-QC

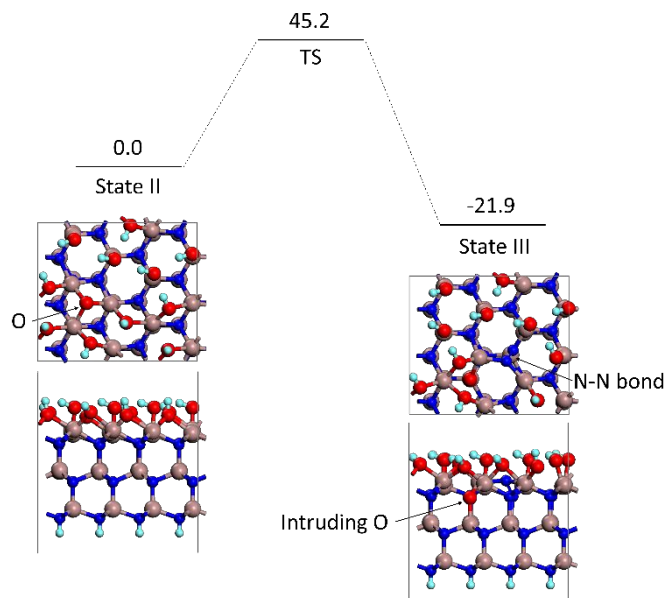
method, the reaction energy from the state II to III is compared with that of the DFT calculations. The stabilized structures of states II and III by the TB-QC method give the reaction energy of -35.5 kcal/mol, indicating an exothermic reaction too and showing qualitative agreement with the DFT calculation results. To further understand the kinetics of this reaction, we calculated the activation energy from state II to state III by using a transition state (TS) search scheme based on a combination of traditional linear and quadratic synchronous transition methods.<sup>44</sup> As shown in Figure 9, the calculated activation energy was 45.2 kcal/mol. This value is somewhat high, indicating that this reaction is normally hard to occur in the absence of external driving force however is possible under the extremely severe friction conditions between the abrasive grain and to-be-polished substrate during the CMP process. Overall, the energetics of the GaN oxidation process revealed by the DFT calculations successfully confirm that the collaboration of chemical reactions with OH radicals and mechanical forces by the abrasive grain is essential for the efficient CMP performance of GaN.



**Figure 8.** Reaction between an OH radical and the fully OH-terminated GaN substrate.

(a) Initial configuration, in which an OH radical was placed on the GaN substrate at a

distance of 2.0 Å. (b) Structure after geometrical optimization using DFT. The upper and lower panels show the top and front views, respectively, of the GaN substrate.



**Figure 9.** Oxidation of the GaN substrate and the corresponding energy change calculated using DFT. The energy units are kcal/mol. The upper and lower panels show the top and front views, respectively, of the GaN substrate.

#### 4. Conclusion

In this work, we performed TB-QCMD simulations to study the CMP process of a GaN (0001) substrate polished by an amorphous SiO<sub>2</sub> abrasive grain, in order to reveal the cooperative roles of chemical reactions and mechanical forces in OH-radical-assisted CMP processes of GaN substrates. Our CMP simulations demonstrate that GaN substrates cannot be polished by SiO<sub>2</sub> without the assistance of OH radicals. However, when OH radicals are continuously added into the system, the removal of N and Ga atoms from the GaN substrate proceeds via the following three reaction steps: (i) first, all of the H terminations on the GaN surface are replaced by OH terminations through continuous

reactions between OH radicals and the GaN surface; (ii) after the GaN substrate is fully terminated by OH groups, the H atoms of the OH terminations are removed from the surface by reacting with newly added OH radicals, which generate H<sub>2</sub>O molecules and leave terminal O atoms with dangling bonds on the surface; and (iii) finally, the residual terminal O atoms intrude into the substrate with concomitant dissociation of Ga–N bonds and generation of N–N bonds, which accumulatively lead to the removal of N and Ga atoms from the substrate. Then by the DFT calculations, we successfully verified the feasibility of the above reactions from an energetic perspective. The results obtained in this work demonstrate that, although it is difficult to polish GaN solely by either chemical reaction with OH radicals or mechanical frictions due to the abrasive grain, the collaborations of the both chemical and mechanical aspects may effectively assist material removal and afford good CMP performance.

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