Mechanochemical reactions of GaN–Al₂O₃ interface at the nanoasperity contact: Roles of crystallographic polarity and ambient humidity

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Abstract: Mechanochemical reactions of the GaN–Al₂O₃ interface offer a novel principle for scientific and technological merits in the micro-/nano-scale ultra-precision surface machining. In this work, the mechanochemical reactions on Ga- and N-faced GaN surfaces rubbed by the Al₂O₃ nanoasperity as a function of the environmental humidity were investigated. Experimental results indicate that the N-face exhibits much stronger mechanochemical removal over the relative humidity range of 20%–80% than the Ga-face. Increasing water molecules in environmental conditions significantly promotes the interfacial mechanochemical reactions and hence accelerates the atomic attrition on N-face. The hypothesized mechanism of the selective water-involved mechanochemical removal is associated with the dangling bond configuration, which affects the mechanically-stimulated chemical reactions via altering the activation energy barrier to form the bonding bridge across the sliding interface. These findings can enrich the understanding of the underlying mechanism of mechanochemical reactions at GaN–Al₂O₃ interface and a broad cognition for regulating the mechanochemical reactions widely existing in scientific and engineering applications.

Keywords: crystallographic polarity; ambient humidity; mechanochemical removal; GaN–Al₂O₃ interface

1 Introduction

Given its wide direct bandgap, excellent mechanical properties, high thermal conductivity, and superior temperature stability, gallium nitride (GaN) has become one of the most promising structural and substrate materials applied in low-energy light-emitting diode [1, 2], high frequency/power microelectronic and optoelectronic devices [3, 4], and high-electron-mobility transistor [5, 6]. High-efficiency, high-reliability, and long-lifespan micro/nanodevices require the non-destructive GaN substrate with subnanometer surface

roughness and global geometric accuracy. Nowadays, the chemical mechanical polishing/planarization (CMP) that utilizes the coupling effect of external mechanical interactions (impact and scratch due to nanoparticles) and chemical reactions (polishing slurries) has emerged as the main processing method for hard-brittle materials to limit lattice defects and achieve global planarization effectively [7–10]. Nevertheless, the lack of fundamental understanding of mechanochemical removal mechanism at the tribological interface severely restricts the further improvement in the accuracy and efficiency of the GaN planarization during the CMP process.

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The actual CMP environment constitutes an extremely complicated tribological system involving the interactions among abrasive particles, polishing slurry, and the wafer surface. Due to the randomly repeated action of multiple abrasive particles and uncontrollable external mechanical interaction, the actual material removal process can hardly be monitored and quantitatively characterized in real-time [11]. Different from the internal property of material, the tribological performance as a system response may change with the environmental parameters (e.g., relative humidity (RH) and temperature), surface properties (e.g., hardness, chemical activity, and atomic structure), and processing parameters (e.g., applied load/pressure, velocity, and processing time) [12–18]. Hence, the well-designed approach is desired to obtain the mechanistic knowledge of the occurrence of mechanically-stimulated chemical reactions between the abrasive nanoparticle and the GaN substrate in the single-asperity contact with precisely controlled contact pressure/area, velocity, reactant concentration, and reaction time.

Based on the pin-disk experiments for GaN film on Al_2O_3 substrate, previous studies indicated that the microscopic material removal behavior of GaN film can be evidently affected by the environmental moisture and the crystal orientation. This phenomenon was speculated to be mainly attributed to the change in the mechanochemical reactions at the frictional interface [19–21]. The shear-induced formation of oxide and hydroxide layers on GaN surface with the aid of water molecules in high humidity conditions distinctly improved the removal rate by two orders of magnitude compared with that in dry air conditions, and the removal process was described as the mechanical abrasive removal of the continuously oxidized layer on GaN substrate. However, the mechanochemical removal and the stress corrosion-induced mechanical removal process are difficult to distinguish under the plastic yield contact situation [22, 23]. Besides, the wurtzite GaN single crystal has a spontaneous polarization along the $\langle 0001 \rangle$ crystal orientation and exhibits two different polar faces with distinct polarization orientations, i.e., Ga-polar (0001) and N-polar (000 $\bar{1}$) crystal faces. Existing studies show that the crystallographic polarity has a prominent effect on the chemical etching, mechanical scratching, and

removal rate of CMP [8, 24–29]. The difference in chemical stability and reactivity with opposite polarities strongly affects the mechanochemical reactions [30]. However, no effort has been made in the previous literature to disclose the atomistic/molecular mechanism of crystallographic polarity dependent mechanochemical reactions at the sliding interface of GaN– Al_2O_3 under the purely elastic contact prior to material yield.

In this study, the mechanochemical reactions were investigated on Ga- and N-faced GaN surfaces rubbed against the Al_2O_3 nanoasperity at different environmental humidity conditions. Experimental results indicate that the crystallographic polarity and the ambient humidity strongly affect the mechanically-stimulated chemical reactions at the GaN– Al_2O_3 interface. In the purely elastic contact, the mechanochemical removal on N-face shows a positive correlation with humidity, whereas Ga-face demonstrates a strong mechanochemical removal resistance over the entire RH range of 3%–80%. Based on the analysis of chemical characterization by using the selected-area X-ray photoelectron spectroscopy (SAXPS) and microstructure observation via the high-resolution transmission electron microscopy (HRTEM), the mechanism of mechanochemical atomic attrition involved in the wurtzite GaN surface was discussed.

2 Materials and methods

2.1 Material preparation

The undoped *c*-plane bulk GaN wafer (Heifei Crystal Technical Material Co., Ltd., China) was used as the substrate in all of the nanoscratching/nanoindentation tests and the nanowear experiments. As-received monocrystalline GaN samples were produced using the hydride vapor phase epitaxy technique and then subjected to double-sided polishing in accordance with the universal CMP protocol. On the basis of the wurtzite crystal structure of GaN, the crystal face perpendicular to [0001] orientation is known as Ga-face, whereas the opposite face (perpendicular to [000 $\bar{1}$] orientation) is N-face, as displayed in Fig. 1(a). Because of the surface oxidation by oxygen and water molecules after the long-term storage in an ambient environment, both the Ga- and N-faced GaN surfaces were covered with a native oxide layer [26]. To eliminate

Fig. 1 Schematic of Ga- and N-faced GaN structures and nanowear tests. (a) Atomic structures of N-faced (N-polarity, left) and Ga-faced (Ga-polarity, right) bulk GaN samples. (b) Mechanochemical removal tests on Ga- and N-faced GaN surfaces with an Al_2O_3 microsphere attached to an AFM system equipped with a home-built humidity control system. The inset shows the scanning electron microscope (SEM) image of the Al_2O_3 microsphere.

the effect of the oxide layer on the mechanochemical reactions at the GaN– Al_2O_3 interface, such native oxide layer on Ga- and N-faced GaN surfaces was removed completely by immersing the samples in 3 wt% hydrofluoric acid (HF) solution for 3 min. Before tribological tests, all the samples were ultrasonically cleaned using acetone, ethanol, and deionized water in sequence, and then dried using pure nitrogen. Using an atomic force microscope (AFM, SPA-300HV Probe Station, Seiko, Japan) with the spatial resolution of 0.2 nm for X – Y plane and 0.01 nm for Z direction, the surface roughness (R_a) of Ga- and N-faced GaN samples was estimated at less than 0.3 nm over an effective sampling area of $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ scanned in a vacuum ($< 10^{-3}$ torr) by a sharp Si_3N_4 probe with the spring constant of 0.1 N/m and a nominal curvature radius R of 20 nm (MLCT, Bruker, MA, USA).

2.2 Nanoindentation and nano scratching experiments

The mechanochemical removal tests on Ga- and N-faced GaN surfaces against the Al_2O_3 microsphere were performed using a humidity-controlled AFM connected to an external atmosphere control system, as displayed in Fig. 1(b). The Al_2O_3 microsphere with a radius R of 2.5 μm was attached to a silicon cantilever with a spring constant of 16.8 N/m. The torsional rigidity of this Al_2O_3 probe was calibrated using the standard sample grating with a trapezoidal structure with a wedge angle of $54^\circ 44'$ (TGF11, Mikro Masch, Germany) [31]. The conic diamond probe (Micro Star Technologies, TX, USA) with R of 0.5 μm and k of 100 N/m was also employed to compare the effect of

counter-surface chemistry on the material removal of GaN surface. The RH in the environment was ranged from 3% to 80% with an error of 2%. The number of reciprocating cycles (N) and sliding velocity (v) were 2,000 and 2 $\mu\text{m/s}$, respectively, and the ambient temperature was kept at $23 \pm 2^\circ\text{C}$. The applied load (F_n) was 4 μN , which provided the maximum Hertzian contact stress of $\sim 1.5\text{ GPa}$ [32]. Nanoindentation tests with a series of penetration depths on Ga- and N-faced GaN surfaces were performed using nanomechanical test instruments (TI750, Hysitron, Bruker, MA, USA) with a Berkovich diamond nanoindenter.

2.3 HRTEM and SAXPS characterization

The microstructures beneath the removal tracks on the N-faced GaN surface were detected using HRTEM (Jeol JEM-2800, Tokyo, Japan). A conductive epoxy polymer layer was deposited on the targeted area before the TEM sample preparation to prevent the possible structural damage caused by Pt deposition and focused ion beam milling (FIB, NanoLab 400, FEL, USA). Chemical compositions of HF-etched pristine surface, worn area, and mechanochemical reactions products on N-faced GaN surface were analyzed using SAXPS (PHI VersaProbe III, Physical Electronics, Inc., MN, USA). The XPS system was equipped with a monochromatic X-ray source, and the minimum spot size of 20 μm was used in Ga 3d and O 1s regions. A dual-beam (electron + ion) was used in the XPS characterization to avoid the electrical charging of the detected sample. The wear debris and track for the XPS characterization were produced on the N-faced GaN substrate against an Al_2O_3 sphere with a diameter

of about 3 mm by using a universal micro-tribotester (UMT-5, Bruker, USA).

3 Results

3.1 Nanowear tests on Ga- and N-faced GaN surfaces at different RHs

The applied normal load is 4 μN in the nanowear tests on Ga- and N-faced GaN surface at different RHs. The corresponding maximum Hertzian contact stress is approximately 1.5 GPa, which is much lower than the plastic yield strength of GaN (~ 15 GPa) [33]. In that case, pure mechanical interactions cannot result in material removal. The reciprocating nanowear tests on Ga- and N-faced GaN surfaces against the Al_2O_3 microsphere were performed in the RH range of 3%–80%. Figures 2(a) and 2(b) display the AFM images and the average cross-sectional profiles of wear tracks produced on Ga- and N-faced GaN surfaces, respectively. The removal depths and volumes as a function of RH are plotted in Fig. 3. In dry air

conditions, the slight wear occurs on Ga-face and N-face, and the difference in removal depths/volumes of wear tracks on these two surfaces is within the statistical discrepancy. As the RH value increases, the removal depth on Ga-face remains constant (~ 0.5 nm), suggesting an independent trend of ambient humidity in the entire RH range of 3%–80%. This result demonstrates that the Ga-faced GaN surface maintains strong mechanochemical wear resistance in humid air. The slight material removal on the Ga-faced GaN surface at different RHs may be attributed to the mechanical removal of a residual native oxide layer with weak mechanical properties. However, the material removal on N-face behaves a remarkably different trend from that on Ga-face under the same sliding parameters. As the RH increases from 3% to 80%, the removal depth on the N-face increases from 0.5 to 3.4 nm, and the removal volume increases nearly by 10 times (from $\sim 10^5$ to $\sim 10^6$ nm 3). The higher material removal rate of N-faced GaN than Ga-faced GaN is consistent with the results obtained in real CMP [8, 28]. Besides, the similar humidity-dependent wear

Fig. 2 AFM images and average cross-sectional profiles of the wear tracks on (a) Ga- and (b) N-faced GaN surfaces produced by sliding the Al_2O_3 tip at different RHs under the conditions of $F_n = 4$ μN , $v = 2$ $\mu\text{m/s}$, $N = 2,000$, and RH = 3%–80%.

phenomenon of N-face was also observed in the macro-tribological tests on the GaN films [20].

The above experimental results indicate that the crystallographic polarity can strongly affect the material removal on GaN surfaces, and the material removal occurs readily on N-face when rubbed by the Al_2O_3 microsphere under the contact stress much lower than the plastic yield of GaN material. Compared with the purely mechanical wear due to plastic deformation and fracture, the contact pressure for material removal is dramatically reduced to less than 1.5 GPa. Considering that GaN is difficult to be chemically reacted with water under the conventional thermodynamics condition, the increase in material removal under high humidity caused by purely chemical corrosion can be ruled out [34], and hence the material removal should be attributed to the mechanically-stimulated chemical reactions at the GaN– Al_2O_3 interface [20], which will be discussed later. The different nanowear behaviors of Ga-face and N-face also show that the material removal here is dominated by the interfacial properties, rather than the bulk material properties. Unlike the direct mechanical interaction, the mechanochemical reaction under the elastic contact that does not reach the plastic limit of GaN material is strictly limited to the outermost layers of the friction interface. This picture has been clarified based on the dynamic molecular simulations for the mechanochemical removal of single crystalline silicon against silica microsphere with water molecules [35]. The removal mechanism underlying the mechanochemical reactions between GaN surface and Al_2O_3 microsphere should be revealed to explore the influencing mechanism of crystallographic polarity.

3.2 Friction force and energy dissipation on Ga- and N-faced GaN surfaces at different RHs

The friction force varied with the reciprocating cycle is recorded during the sliding process at different RHs to investigate the effects of crystallographic polarity and humidity on the frictional behaviors of GaN surface, as shown in Fig. 4. The friction force value was calculated using the reverse voltage times torsional rigidity of the AFM probe that was calibrated by the standard sample grating with the trapezoidal structure [31]. The error bar was obtained through the standard deviation from three individual measurements. All of the friction force curves experience a period of initial running-in process and then gradually decrease to a stable value with increasing reciprocating sliding cycles. The reduction in friction force is mainly attributed to the decreasing contact pressure after the rough asperities on pristine friction pair surfaces are flattened [36]. The humidity dependence of friction forces at the initial and the final steady states indicates that the chemical and/or physical conditions of the interfaces dynamically changed over the entire RH range. Water molecules from the ambient environment adsorb readily on GaN surfaces and provide a lubricating film with low shear strength to prevent direct solid–solid contact [20, 37]. As the RH increases, the thickened adsorbed water film enhances the lubricating performance and results in a stable and relatively low friction state [14]. In general, the friction forces on N-face have higher initial and final stable values compared with those on Ga-face.

Notably, the friction forces on Ga- and N-faced surfaces show humidity dependence, but only the wear behavior on N-face increases considerably with

Fig. 3 (a) Removal depth and (b) volume of wear tracks on Ga- and N-faced surfaces produced by a sliding Al_2O_3 tip as a function of RH under the conditions of $F_n = 4 \text{ }\mu\text{N}$, $v = 2 \text{ }\mu\text{m/s}$, $N = 2,000$, and $\text{RH} = 3\%–80\%$.

Fig. 4 Friction forces on (a) Ga-face and (b) N-face as a function of sliding cycle under the conditions of $F_n = 4 \mu\text{N}$, $v = 2 \mu\text{m/s}$, and $\text{RH} = 3\%–80\%$.

increasing humidity. Generally, the material removal is related to the frictional dissipated energy at the tribological interface [38–40]. The variation trends of the dissipated energy and removal rate as a function of RH are compared to explore the relationship between interfacial energy dissipation and material removal of N-face (Fig. 5). The frictional dissipated energy is calculated using the integration of the friction force (Fig. 4(b)) over the entire reciprocating sliding process, and the removal rate is determined by dividing the removal volume (Fig. 3(b)) with the frictional work [41]. A negative correlation between the frictional energy dissipation and the removal rate for the N-faced GaN surface is observed. The disparity between the total dissipated energy and the removal rate at 80% RH has reached the maximum. Results suggest that increasing the ambient humidity can improve the lubrication capability for the tribological interface, but expedites the mechanochemical reactions, thereby promoting the material removal of N-face. Thus, even in the

lubricated state, the external mechanical energy required for the interfacial mechanochemical reactions between N-faced GaN substrate and Al_2O_3 counter-surface is sufficient for all of these selected RH conditions.

4 Discussion

4.1 Nanoindentation and nanoscratching on Ga- and N-faced GaN surfaces

Given that the mechanical properties are the direct factors to dominate the material removal behavior under normal circumstances, the difference in mechanical properties (e.g., elastic modulus and hardness) between Ga- and N-faced GaN substrates should be verified, so as to evaluate the influence of mechanical properties on the material removal behavior. Figure 6 compares the elastic modulus and the hardness of Ga- and N-faced GaN surfaces at varying indenter penetration depths. This result shows that both the elastic modulus and the hardness initially increase and then gradually stabilize with increasing penetration depth [42]. No obvious difference was observed between the estimated elastic modulus and hardness values of Ga- and N-faced GaN surface at the stabilized period (with the penetration depth of $\sim 20 \text{ nm}$). Since the elastic modulus and hardness of Ga- and N-faced surfaces are always close for the given penetration depth, the mechanical property should not be the key factor that leads to the different material removal behaviors between these two GaN substrates with different polarities.

Previous studies revealed that, even in the purely elastic contact region, the mechanical shear stress can promote surface damage by accelerating the hydrolysis

Fig. 5 Correlation of the total frictional dissipated energy of the GaN– Al_2O_3 interface and averaged material removal rate over the 2,000 reciprocating sliding cycles on N-faced GaN surface at various RHs.

Fig. 6 Mechanical properties on GaN surfaces determined using nanoindentation tests. Estimated (a) elastic modulus and (b) hardness as a function of penetration depth on Ga- and N-faced GaN surfaces. The error bar is the standard deviation from three individual measurements.

reaction of the chemical bonds of the substrate, which is called stress corrosion [22, 43]. To verify whether the promotion of environmental water content on the removal rate of N-face is attributed to stress corrosion, the nanowear tracks were produced in dry air and high humidity conditions using the diamond AFM tip, where the contact pressures under these two conditions were the same and much lower than the plastic yield of GaN. Since the GaN/diamond pair is chemically inert, the interfacial mechanochemistry in the tribological process can be ruled out. To obtain a similar loading situation as shown in the Al_2O_3 case (Fig. 2), a normal load of $0.5 \mu\text{N}$ was applied by the diamond tip with a diameter of $1 \mu\text{m}$, and thereby a contact pressure of 1.9 GPa was provided. Figure 7

shows the *in-situ* AFM images and average cross-sectional profiles of the wear tracks produced on N-face using the diamond tip at 3% and 80% RHs. The negligible difference in wear depth and volume indicates that the role of stress corrosion in removing N-face under high humidity is extremely limited and the slight surface wear less than 0.5 nm in depth may be mainly attributed to the mechanical removal of outermost native oxide layer. Results suggest that the counter-surface is involved in the chemical reactions to stimulate the material removal on N-face. In other words, the combination of chemically active counter-surface and external mechanical stress is the necessary condition for the surface material removal in the elastic contact region.

Fig. 7 AFM images of wear tracks on N-faced GaN surface against the diamond tip with a nominal radius of $1 \mu\text{m}$ at (a) 3% and (b) 80% RHs. $F_n = 0.5 \mu\text{N}$, $v = 2 \mu\text{m/s}$, and $N = 2,000$.

4.2 Role of mechanochemistry in the material removal of N-faced GaN surface

The microstructures underneath the worn track produced by the Al_2O_3 microsphere at 60% RH were characterized using HRTEM to investigate the material removal mechanism of the N-faced GaN surface under the elastic contact. Considering the accuracy of positioning and the convenience of TEM operation, a detecting nanochannel with a depth of about 17 nm along a $\langle 10\text{--}10 \rangle$ direction was obtained on N-face by performing 6,000 reciprocating sliding cycles under the sliding conditions of $F_n = 4 \mu\text{N}$ and $v = 10 \mu\text{m/s}$. Figure 8 displays the (a) AFM image, the (b) cross-sectional profile, and the (c) HRTEM image of the crystal lattice labeled by the red frame in (b) after the mechanochemical removal process. Due to the thermal drift of AFM equipment, the scratched area appears rough after a long period of the reciprocating sliding process. No evident crystal dislocations and lattice distortion are observed in the subsurface layer of the entire detection portion of the scratched area regardless of the surface roughness. Considering that the curvature radius of the scanned AFM tip is approximately 20 nm, the scanned area with a relatively low depth–width ratio is difficult to characterize, resulting in that the real worn profile (HRTEM image in Fig. 8(c)) cannot

be accurately represented by AFM imaging (Fig. 8(b)). Results suggest that the severe material removal is not due to the mechanical interaction and may originate from the mechanochemical reactions with the assistance of water molecules and the chemically active Al_2O_3 tip. Chemically, the contribution of mechanical action during the material removal process is not to remove material directly via plastic fracture or extrusion, but to input mechanical energy for stimulating the mechanochemical reactions at the GaN– Al_2O_3 interface.

Based on the following Hertz contact model [44], the maximum penetration depth (d) at the given normal load F_n of 4 μN on N-face against Al_2O_3 microsphere with a radius R of 2.5 μm can be estimated as lower than 0.5 nm (2–3 atomic layers of GaN crystal),

$$d = \left[\frac{9(F_n)^2}{16R(E^*)^2} \right]^{1/3} \quad (1)$$

where E^* is the combined elastic modulus expressed by $E_1 E_2 / [(1 - \nu_1^2)/E_2 + (1 - \nu_2^2)/E_1]$; E_1 (E_2) and ν_1 (ν_2) are the elastic modulus and the Poisson's ratio of Al_2O_3 (N-face), respectively. Hence, the mechanochemical interactions only occurred at the outermost layers of the GaN/ Al_2O_3 interface, and the atomic layers of the bulk material inside remained intact. Material removal

Fig. 8 (a) Top- and (b) cross-sectional view (obtained along the red dashed line in (a)) AFM images of wear track on N-faced GaN surface produced by the Al_2O_3 microsphere under the conditions of $F_n = 4 \mu\text{N}$, $v = 10 \mu\text{m/s}$, RH = 60%, and N = 6,000. (c) HRTEM image of the worn area taken from the red frame in (b).

of N-face by sliding the Al_2O_3 microsphere under such mild reaction conditions can avoid the crystal lattice distortion and dislocation in the subsurface, which can be usually produced by mechanical interactions and detected beneath the removal track [45]. The mechanochemical reactions that occur in several atomic layers of the contact interface should be responsible for the significant difference in the mechanochemical removal behaviors of Ga- and N-faced GaN surfaces.

The elemental compositions and the chemical states of wear debris and track generated at 40% RH were characterized by SAXPS to further investigate the role of mechanochemical reactions in the material removal of N-face under ambient conditions. Given that the wear track produced by Al_2O_3 microsphere in AFM tests (wear track size normally less than $1,000 \text{ nm} \times 300 \text{ nm}$) is difficult to be detected due to the limited spatial resolution, the following wear track and debris for the SAXPS characterization were prepared using a bigger Al_2O_3 sphere with a diameter of about 3 mm (as mentioned in Section 2.3). The applied load and the corresponding contact pressure were respectively controlled at 0.5 N and 1.05 GPa to suppress mechanical damage of GaN substrate. Figure 9(a) shows the O 1s spectra of wear debris and tracks produced at 40% RH. Here, the characterized results of wear debris produced at 80% RH and the pristine GaN surface (HF-etched N-face) are presented for comparison. The wear track produced at 40% RH exhibits a more intensely O 1s peak structure than that of the pristine surface, indicating the formation of a thin oxidized layer (Ga_xO_y -like structure) due to

the mechanochemical reactions during the tribological process. The detected O 1s signal on the pristine surface may be attributed to the inevitable oxide adsorption and residual oxygen in the XPS chamber. The wear debris with higher oxygen intensity than the wear track at 40% RH suggests that strong shear-assisted oxidation reactions should be accompanied during the material removal on N-faced GaN surface and the wear debris is the chemical product of the oxidation reactions, rather than the chips or fragments of mechanical removal on GaN substrate. Moreover, the oxygen intensity of the oxidation products produced at 80% RH further increases, revealing that a series of more violent chemical reactions occurs at the sliding interface in an environment with high water content. The above results indicate that the oxygen intensity of wear debris is closely correlated with the ambient humidity of the tribological environment. Water molecules play a vital role in the mechanochemical chemical reactions, and this result is consistent with the material removal results under the GaN– Al_2O_3 nanoasperity contact (as evidenced in Fig. 3).

Figure 9(b) shows Ga 3d spectra of wear debris and tracks formed at 40% RH and wear debris produced at 80% RH compared with a newly HF-etched GaN surface. Different from a narrow Ga 3d peak at 19.7 eV for the pristine GaN surface, the little broader peaks were observed from the wear track (at 20.0 eV) and wear debris (at 20.2 eV) formed at 40% RH [45]. The appearance of a broad peak may be caused by the heterogeneous structure consisting of Ga–O and Ga–N bonds [26]. Furthermore, the blue shift in Ga 3d spectra can be observed at the wear track and debris compared

Fig. 9 (a) O 1s and (b) Ga 3d SAXPS spectra for the wear debris and wear track produced on N-faced GaN surface by sliding an Al_2O_3 sphere at 40% RH. The pristine HF-etched GaN surface and debris produced at 80% RH are added for comparison.

with the pristine surface, and the degree of the peak shift exhibits a positive correlation with the intensity of the interfacial mechanochemical reactions. The Ga 3d peak of wear debris further shifts to 20.4 eV as the RH goes up to 80%. Thus, it can be speculated that the atomic attrition of N-face is mainly caused by the water-involved interfacial mechanochemical reactions with the aid of the chemically active sliding tip (Al_2O_3), and these reactions demonstrate significant crystallographic polarity and ambient humidity dependences. Besides, no Al element signal was captured in the SAXPS spectra, revealing scarcely that any wear has occurred on the Al_2O_3 sphere that participates in the interfacial chemical reactions.

4.3 Crystallographic polarity dependent mechanochemical reactions at the GaN– Al_2O_3 interface

It has been demonstrated that the GaN substrate exhibits strong resistance to material removal when the compressive and the shear stresses are applied using the diamond counter-surface, but not when the Al_2O_3 is used. Given that the crystal lattice constants of sapphire (being mainly composed of Al_2O_3) and GaN are relatively close to form Al–O–Ga bonds, sapphire has been widely used as the substrate of GaN epitaxial devices [37]. Previous studies suggest that the active Al_2O_3 microsphere may promote the atomic attrition of the N-faced GaN substrate by forming bonding bridges (i.e. Al–O–Ga) in watery environments during the friction process [20, 45]. Here, the topmost

layer of the N-faced GaN surface is assumed as the Ga atomic layer, as shown in Fig. 10(a). When the Al_2O_3 counter-surface and the N-face are exposed to ambient air, the topmost layers of these two surfaces react readily with water molecules and form Ga/Al–OH bonds [46, 47]. When the friction pair surfaces terminated with hydroxy groups get into contact with each other, the “Al–O–Ga” bonding bridges form at the tribological interfaces via dehydration condensation reactions, providing tensile or shear stress to stimulate the hydrolysis reactions of neighboring Ga–N bonds during the relative motion process. Given that the dissociation energy of the Ga–N bond (212 kJ/mol) is smaller than the Ga–O bond (285 kJ/mol) [48, 49], the Ga–N bond is more likely to break than the Ga–O bond, resulting in the removal of the Ga atomic layer from the substrate.

After the first Ga atomic layer has been removed through the mechanically-stimulated chemical reaction induced by the Al_2O_3 microsphere rubbing, the N atoms-terminated N-face is produced, as shown in Fig. 10(b). Every fresh N atom with only one dangling bond is easily accessible to the hydroxide ions of water molecules in ambient air and the outermost layer is gradually hydroxylated [50]. Since N atoms are more chemically inert than Ga atoms, the hydroxylation reactions cannot proceed as fully as the Ga atomic layer, resulting in the coexistence of OH- and H-terminated groups on the topmost layer of the N atoms terminated N-face [46]. Once again, the N atomic layer

Fig. 10 Mechanochemical reactions at the GaN– Al_2O_3 interface in watery conditions. (a) Ga-terminated N-face; (b) N-terminated N-face; and (c) N-terminated Ga-face.

is completely removed through a series of chemical procedures on the basis of the formation of the bonding bridge across the sliding interface and the dissociation of Ga–N bonds in the substrate. The substrate surface returns to the Ga atoms-terminated N-face and the mechanochemical reaction continues in accordance with the same scenario shown in Fig. 10(a). Consequently, the N-faced GaN surface can be continuously removed layer by layer via the mechanically-stimulated chemical reactions. As a sharp contrast, after the Ga layer has been mechanochemically removed as mentioned above (Fig. 10(a)), the Ga-faced GaN surface is converted into N atoms termination, as shown in Fig. 10(c). Different from the single dangling bond of every N atom in Fig. 10(b), the triple dangling bonds occupy the N-terminated Ga-faced GaN surface, that is, every exposed N atom on Ga-face has three dangling bonds. Due to the large repulsion between hydroxide ions and triple dangling bonds, hydroxide ions (from water molecules and Al_2O_3 microsphere) can hardly reach the N atoms-terminated Ga-faced GaN substrate, which strongly suppresses the formation of bonding bridges between the substrate and the sliding counter-surface [24, 51, 52]. As a result, the mechanochemical reaction no longer occurs at the sliding interface. Thus, such Ga-faced GaN substrate exhibits strong resistance to the mechanochemical removal. Given that the same Ga–N bond of the substrate is broken during the above-mentioned mechanochemical removal process, almost no difference exists in the activation energy barrier for the rupture of Ga–N bonds in different atomic structures. Therefore, the dangling bond configuration of N atoms on the topmost layer is emphasized to play an important role in the selective mechanochemical reactions by altering the activation energy barrier to form the bonding bridge, regardless of the surface terminated with Ga or N atom.

5 Conclusions

In this study, we investigated the mechanochemical reactions on Ga- and N-faced GaN surfaces rubbed by Al_2O_3 nanoasperity as a function of environmental humidity. Experimental results indicate that the crystallographic polarity and the ambient humidity strongly affect the mechanically-stimulated chemical

reactions at the GaN– Al_2O_3 interface. The N-face exhibits much stronger mechanochemical removal over the entire RH range of 20%–80% than the Ga-face. The increasing water molecules in environmental conditions can significantly promote the interfacial mechanochemical reactions and hence accelerate the material removal on the N-face. Taking the dangling bond configuration on the polar GaN surface into account, the appropriate mechanism of the selective water-involved mechanochemical reactions is proposed. Given the large repulsion between hydroxide ions and triple dangling bonds, the N atom-terminated topmost layer on the Ga-face suppresses the mechanochemical removal by improving the activation energy barrier to form a bonding bridge across the sliding interface. These findings can advance the understanding of the underlying mechanism of mechanochemical reactions at the GaN– Al_2O_3 interface and provide fundamental knowledge to optimize the ultra-precision surface manufacturing of GaN.

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