Interplay between counter-surface chemistry and mechanical activation in mechinaochemical removal of N-faced GaN surface in humid ambient

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ABSTRACT
Mechanical activation in mechanical removal of GaN using diamond tip and mechanochemical removal using Al 2 O 3 tip are described by the Archard equation and mechanically assisted Arrhenius-type kinetic model, respectively. Evident material-removal under elastic contact occurs with the assistance of interfacial mechanochemical reactions. By analyzing the mechanochemical reactions with Arhrenius-type kinetic model and Hertzian contact mechanics, the critical activation volume and activation barrier are determined semiquantitatively. The mechanical activation originating from the chemically active counter-surface facilitates the mechanochemical atomic attrition by altering the energy barrier of the reaction kinetics. This work can provide deep insights into the mechanochemical-removal mechanism of GaN.

1. Introduction

Gallium nitride (GaN) has superior properties, particularly a wide direct bandgap, low dielectric constant, high breakdown electric field, excellent chemical stability, and high thermal conductivity. Thus, GaN is eliciting great interest because of its broad application prospects in optoelectronic devices and microelectronic devices, such as low-energy light-emitting diodes, electronic devices with high frequency/power/temperature, and short-wavelength emitters/detectors [1–6]. Various forms of surface damages such as crystal distortion, microcracking, and amorphization layer are produced during surface machining process, and they strongly affect the working stability and limit the service life of nanodevices. The process of chemical mechanical polishing/planarization (CMP), which exploits the coupling effect of external mechanical interaction and chemical reaction, has become the most popular ultraprecision machining approach for large-scale surfaces with nanometer-level global geometric accuracy, subnanometer-level surface roughness, and nondestructive surface/subsurface [7–10]. Due to the lack of the scientific understanding of the nanoscale GaN materials’ removal mechanism dominated by the mechanochemical interactions across the tribological interface, the further improvement in the accuracy and efficiency of the surface planarization is severely restricted.

Actual CMP process is associated with an extremely complicated tribological behavior including the interactions among abrasive particles, polishing slurry, and wafer surface [7–11]. The material-removal behavior on the wafer surface is closely related to such tribological components in CMP process, rather than to the intrinsic characteristics of the material [12–15]. Many studies have indicated that the macro/microscopic removal behaviors dominated by mechanochemical interactions are strongly affected by the loading parameters (e.g., load/pressure, velocity/reaction time, and sliding direction), environmental conditions (e.g., humidity, temperature), and surface properties (e.g., bonding energy, chemical activity, particle size, roughness, and mechanical properties) [11–19]. Despite the above studies, the mechanism of mechanochemical reactions on GaN surface is still far from being fully understood because of the uncertain loading conditions in multi-asperities contacts. To fundamental comprehend the physicochemical processes in the CMP of GaN surface, a well-designed approach in a single-asperity sliding contact with the precisely controlled contact pressure/area, velocity, reactant concentration, and reaction time, should be applied.
Previous studies have demonstrated that the material removal using a diamond tip is dominated by the mechanical deformation caused by phase transformation, plastic flow, brittle fracture, and dislocation formation [20–23]. In this case, the material wear can be empirically described by the classical Archard equation, in which the removed volume is proportional to the applied load and inversely proportional to the material hardness [24,25]. Meanwhile, after introducing the chemically active counter-surface and ambient medium, the material removal can be realized through the interfacial mechanochemical reactions under the purely elastic contact, where the contact pressure is far below the plastic yield strength of a material [26]. Experimental and computational results show that the mechanochemical reactions at the frictional interfaces, which involve the formation of interfacial bonding bridges and the rupture of chemical bonds on the substrate, are considered as mechanochemically activated [26,27]. In this case, the chemical reactions are directly initiated by the external mechanical energy that can be propagated through the bonding channel connected with the counter-surface. It provides alternative chemical-reaction coordinates involving a series of different transition states and a reduction in activation energy. The mechanical activation in this reaction processes does not follow the traditional material-removal theory but can be described by the mechanically assisted thermal activation model. The latter is well applied in the mechnochemical removal of Si, GaAs, and diamond-like carbon materials, as well as the interfacial polymerization reactions [28–31]. Nevertheless, no efforts have been made on monocrystalline GaN surface to reveal the contribution of mechanical activation in mechnochemical reactions coupled with the assistance of a chemically active counter-surface at the tribological interface.

Because of the non-reverse crystallographic symmetry along the c-axis direction, c-plane wurtzite GaN can be divided into Ga-faced GaN and N-faced GaN. Up to now, the application of Ga-faced GaN is relatively mature in market, while the N-faced GaN has shown huge application potential in high power and optoelectronic devices due to its particular properties [32–35]. Due to the difference in surface dangling-bond configuration, the surface chemical properties of Ga- and N-faced GaN materials are quite different, e.g., the Ga-face is more chemically inserts than N-face. This difference results in the different material removal rate in CMP processing between these two faces [8,36,37]. Previous studies have demonstrated that N-faced GaN surface exhibited much stronger mechanochemical reaction than Ga-faced GaN surface when rubbed against Al2O3 counter-surfaces [38]. Nevertheless, the interplay between counter-surface chemistry and mechanical activation in mechnochemical material-removal on N-faced GaN surface, which is of great significance for further understanding of the nanoscale material-removal mechanism of monocrystalline GaN, remains unclear.

In the current work, the material-removal behaviors of the N-faced GaN surface against diamond and Al2O3 tips are comparatively studied by using atomic force microscopy (AFM). The mechanical activation in the mechanical removal (the diamond counter-surface) and the mechnochemical removal (the Al2O3 counter-surface) of the N-faced GaN surface are described by the Archard equation and mechanically assisted Arrhenius-type kinetic model, respectively. The mechanism involved in the mechnochemical atomic attrition on the N-faced GaN surface is discussed on the basis of chemical and microstructure characterization using selected-area X-ray photoelectron spectroscopy (SAXPS) and high-resolution transmission electron microscopy (HRTEM).

2. Materials and method

2.1. Material preparation

The undoped c-plane monocrystalline GaN wafers with a thickness of 0.36 mm were purchased from Hefei Crystal Technical Material Co., Ltd., China. These bulk GaN samples with Ga- and N- two faces were prepared on GaN homogeneous substrate using hydride vapor phase epitaxy (HVPE) method and were double-sided polished using CMP technique. We used the N-faced GaN surface to carry out the nanowear tests against the Al2O3 microsphere (tip) or diamond tip, as shown in Fig. 1. The as-received N-faced GaN surface was covered with a ~4 nm-thick native oxide layer (Ga2O3-like structure) according to variation of oxygen concentration with sputter depth by using the Auger electron spectrum (AES, PHI-700, ULVAC-PHI, Inc., Kanagawa, Japan), as shown in Fig. S1 of Supporting Information. Such an oxide layer was formed during the exposure in the atmospheric environment [39,40]. To eliminate the influence of the oxide layer in the material removal behavior (see Fig. S2 in Supporting Information, the result suggests that the oxide layer can promote the material removal), the GaN sample was treated with 3 wt.% diluted hydrofluoric acid (HF) solution for 3 min to remove the oxide layer before nanowear tests. Then, the GaN surface was sequentially subjected to ultrasonic cleaning in ethanol, rinsed with deionized water, and dried under pure N2 gas. The surface topography of the freshly HF-etched GaN surface was characterized with an AFM system (SPA-300HV Probe Station, Seiko, Japan) and the roughness value was estimated at approximately 0.3 nm over the effective sampling area of 10 μm × 10 μm (see Fig. S3 in Supporting Information).
was a spherical Al$_2$O$_3$ tip under the conditions of $F_n = 0.5-5 \mu N$, RH = 60%, $N = 3000$, and $v = 2 \mu m/s$. Comparison of (b) removal depth and (c) removal volume of wear tracks varied with normal load.

2.2. Nanowear tests

All nanowear tests were performed with the AFM system combined with a home-built humidity-control system (see Fig. S4 in Supporting Information). The external system is described in detail elsewhere [41]. More details about the nanowear procedures can be found in Supporting Information. Two types of AFM probes were used in this study to reveal the effect of counter-surface chemistry on GaN material removal. One was a spherical Al$_2$O$_3$ probe with a nominal radius $R$ of approximately 2.5 $\mu$m attached to a cantilever with a force constant $k$ of approximately 19.8 N/m. The other was a conic diamond probe with $R \approx 20$ nm and $k \approx 100$ N/m. Reciprocating nanocratching experiment was performed with a sliding amplitude of 1 $\mu$m by controlling the applied load ($F_n$) to range within 0.5–5 $\mu$N for the Al$_2$O$_3$ probe and 1–25 $\mu$N for the diamond probe. Sliding speed ($v$) varied within 0.1–1000 $\mu$m/s, the relative humidity (RH) varied within 3%–80% (with an error of 2%), and the ambient temperature was maintained at 25 $\pm$ 2 °C. After nanowear tests, all the wear scars were imaged by using a sharp Si$_3$N$_4$ probe (MLCT, Bruker, Billerica, MA, USA) with $R \approx 20$ nm and $k \approx 0.1$ N/m in a vacuum condition of about $10^{-4}$ torr.

2.3. HRTEM and XPS characterization

The atomic structures beneath the wear tracks on GaN substrates produced by Al$_2$O$_3$ and diamond tips were characterized with a TEM system (Jeol JEM-2800, Tokyo, Japan) equipped with an energy-dispersive X-ray (EDX) spectrometer. TEM-EDX cross-section elemental maps of worn track scratched by diamond tip were used to analyze the distribution of chemical composition. A conductive polymer protective layer was deposited onto the TEM sample before Pt deposition and focused ion beam (FIB, Helios NanoLab 400, FEI, Hillsboro, OR, USA) milling to prevent possible structural damage. To investigate the material-removal mechanisms of GaN surfaces against Al$_2$O$_3$ and diamond counter-surfaces, the chemical states and elemental compositions of pristine surface and wear debris were analyzed by SAXPS (PHI VersaProbe III, Physical Electronics, Inc., MN, USA). More details about the XPS characterization can be found in Supporting Information. The wear debris for the XPS characterization were produced by using an Al$_2$O$_3$ sphere with a diameter of 3 mm and a fixed-abrasive pellet with diamond particle ($R = 10-20 \mu m$) by using a universal micro-tribotester (UMT-5, Bruker, Billerica, MA, USA) under the sliding speed of 2 mm/s. The applied load/corresponding maximum Hertzian contact pressure) provided by Al$_2$O$_3$ sphere and diamond particle were controlled at 0.5 N/1.05 GPa and 0.5 N/beyond the plastic yield, respectively.

3. Results and discussion

3.1. Nanowear behaviors of GaN surface against Al$_2$O$_3$ and diamond tips

To explore the material-removal behavior of the GaN surface, a spherical Al$_2$O$_3$ probe with $R \approx 2.5 \mu m$ was driven to rub the substrate under different applied loads. Based on Hertzian contact mechanics, the $F_n$ within the range of 0.5–5 $\mu$N provided the maximum pressure varied from 0.75 GPa to 1.70 GPa at the GaN–Al$_2$O$_3$ sliding interface. Fig. 2a displays the AFM images of wear tracks and the corresponding average cross-sectional profiles after 3000 reciprocating sliding processes at 60% RH. The removal depths and volumes as a function of normal load were compared in Fig. 2b and c. The critical load was 1.5 $\mu$N for the material removal under the above sliding conditions. The corresponding contact pressure can be calculated as about 1.1 GPa, which was far below the plastic yield of GaN (~15 GPa) [42]. Based on the previous studies, the atomic attrition behavior before the plastic deformation may be due to the mechnochemical reactions that occur at the tribological interface, rather than to purely mechanical interactions. No obvious surface damage can be detected within the spatial resolution of AFM until the load was increased to 1.5 $\mu$N. With subsequently increased applied load to 5 $\mu$N, removal depth and volume significantly increased from 0.4 nm to 4.3 nm and from $0.3 \times 10^8$ nm$^3$ to $1.4 \times 10^9$ nm$^3$, respectively. However, under the elastic contact against the diamond tip with a nominal radius of 1 $\mu$m (Hertzian contact pressure $\approx$ 1.9 GPa), the material removal cannot occur through purely mechanical interaction under dry and high-humidity conditions (see Fig. S5 in Supporting Information). The critical contact pressure for the material-removal process may also be related to the activation energy of the chemical reactions that can be triggered by the mechanical action between GaN substrate and Al$_2$O$_3$ counter-surface. When the imposed frictional
energy overcame the reaction activation energy, the material wear can occur on the GaN surface with the assistance of the mechanical shear of the Al$_2$O$_3$ tip.

Removal volume ($V$) as a function of normal load ($F_n$) did not follow the Archard wear equation developed by the classical plastic removal model [43], as follows:

$$V = k F_n L H,$$

(1)

where $H$ is the hardness of GaN material (~20 GPa), $L$ is the sliding distance, and $K$ is the wear coefficient of the tribo-system. In the GaN-Al$_2$O$_3$ case, material removal under a purely elastic contact state should be dominated by the synergy effect of chemical reactions and mechanical interactions. To compare the material removal governed by mechanical actions, a diamond tip was used to rub GaN substrate under normal loads of 1–25 μN, where the maximum corresponding contact pressure exceeded the value within the elastic-deformation range. Fig. 3 shows the AFM images of wear tracks, as well as the corresponding average cross-sectional profiles and the variations in removal depth and volume with different normal loads. Results indicated that GaN material can be removed within the entire load range. As the load increased from 1 μN to 25 μN, the wear depth and volume increased from 1.3 nm to 12.1 nm and from 1.0 × 10$^5$ nm$^3$ to 1.1 × 10$^6$ nm$^3$, respectively. The mechanical removal rate at 25 μN ($2.4 \times 10^{-12}$ m$^3$/N-m) was about 20 times of the mecanochemical removal rate at 5 μN ($4.5 \times 10^{-14}$ m$^3$/N-m). In the case of using the diamond tip, the removal volume was proportionatal to the load when $F_n > 1$ μN. The wear coefficient $K$ for the tribological system was estimated to be 0.005 according to Eq. (1). These results demonstrated that the Archard theory can well predict the material-removal behavior dominated by plastic deformation or ploughing effect but failed to quantify the material removal of GaN induced by mechanically stimulated chemical reaction (Fig. 2).

### 3.2. Chemical state and microstructures analyses of wear track on GaN surface

The above results showed that by combining chemically active counter-surface and external mechanical stress, GaN material can be removed through mecanochemical reactions in the elastic contact region, where the material removal should not introduce the lattice damage into the subsurface. The chemical states of wear debris were characterized by SAXPS to further confirm the removal mechanism of GaN substrate against Al$_2$O$_3$ counter-surface, as shown in Fig. 4. Considering that the wear track produced by Al$_2$O$_3$ AFM tip cannot be detected due to the limited spatial resolution, the following wear debris for SAXPS characterization was prepared with an Al$_2$O$_3$ sphere having a diameter of 3 mm by using UMT-5 tribo-tester (the selected measurement location is shown in Fig. S6 of Supporting Information). To suppress the mechanical damage of the GaN substrate, the applied load and the corresponding contact pressure were controlled at 0.5 N and 1.05 GPa, respectively. As a reference, the O 1s and Ga 3d XPS spectra of the pristine HF-etched GaN surface was added for comparison.
pristine GaN surface and the wear debris produced by using the diamond particles were also plotted. The wear debris produced by the Al₂O₃ sphere at 40% RH showed a more intense O 1s peak structure than that of the pristine surface. The O 1s spectrum is decomposed into three components at 530 eV, 531.5 eV, and 533.1 eV, which can be assigned to chemisorbed oxygen atom, gallium oxide (Ga–O), and hydroxide, respectively [7,44]. Wear debris with higher O 1s intensity suggested that shear-assisted oxidation reactions were accompanied during the material removal process and the wear debris was the chemical product of oxidation reactions with GaₓOᵧ-like structure. The symmetric O 1s peak at the position of 531.5 eV on pristine HF-etched GaN surface shows that the detected O 1s signal may be attributed to the residual

![Fig. 5. Cross-sectional HRTEM image of the wear track produced on GaN surface using Al₂O₃ tip with a radius of ~2.5 μm under the condition of \( F_n = 4 \, \mu N, \text{RH} = 60\%, N = 6,000, \) and \( v = 10 \, \mu m/s. \)]
oxide after HF-treatment. As a comparison, the chips or fragments of mechanical removal by diamond particle showed a hydroxide component. In general, wear debris is easier to oxidize due to the amorphous structure, where the local Ga–N bond is elongated and the bond energy is weakened.

Accordingly, Ga 3d peak is deconvoluted into three components at binding energy of 20.5–20.7 eV (Ga2O3/Ga–OH), 19.7 eV (Ga–N), and 18.4 eV (Ga-Ga/metallic Ga) [7,44]. The oxide peak of debris produced by diamond shows a similar spectrum as that of pristine HF-etched GaN surface, which demonstrates a limited mechanochemical reaction at the GaN-diamond interfaces. The debris produced by Al2O3 microsphere shows a higher oxidized component compared with these two and displays a peak shift (rightward) of the Ga–O/Ga–OH peak may be due to the heterogeneous oxidized structure. Thus, the ratio of oxidized Ga peak area to Ga 3d peak area (A_{GaO/Ga–OH}/A_{Ga2O3}) was increased from 0.24 (pristine HF-etched GaN) and 0.30 (debris produced by using diamond) to 0.45 (debris produced by using Al2O3). Combined with the results of previous studies, the chemically active Al2O3 microsphere may promote the atomic attrition of GaN substrate by forming bonding bridges (i.e., Al–O–Ga) in wet environments [13,45] during the slight rubbing process. We hypothesized that the strained stress and mechanical energy were propagated to the GaN substrate through the interfacial bonding bridges, resulting in an effectively decreased activated energy of water-involved bonding rupture of the GaN crystal structure. Additionally, no Al element signal was observed in the SAXPS spectra, revealing scarcely any wear occurred on the Al2O3 sphere involved in the interfacial mechanochemical reactions.

Fig. 5 displays the cross-sectional HRTEM image of the local microstructure underneath the wear track. This wear track (groove) with a depth of ~11 nm and a width of ~900 nm on GaN surface was produced by performing 6000 reciprocating rubbing processes against the Al2O3 tip under the maximum Hertzian contact pressure of 1.5 GPa. More TEM-observation details including the location of the entire detection area can be found in the Supporting Information (Fig. S7–S9). Although the wear surface was slightly rough, no dislocations and plastic slippage can be observed throughout the entire detection portion of the scratched area, and the subsurface of GaN nanochannel maintained the wurtzite lattice structure. The nondestructive surface resulted from the mechanochemistry-induced atomic attrition under mild thermodynamic conditions. According to the Hertzian contact mechanics, the maximum penetration depth of the Al2O3 microsphere was estimated to be less than 0.25 nm (1–2 atomic layers of GaN) under the critical normal load of ~1.5 μN, as shown in the measurement results Fig. 2. The interfacial mechanochemical reactions stimulated by the shear action of Al2O3 microsphere strictly involved the atoms of the topmost surface in the nanosapphire contact area, whereas the underlayer of the GaN substrate was intact. In this case, the crystal lattice was not damaged by the ultralow contact pressure.

The diamond tool/tip is extensively used in ultra-precision manufacturing due to its excellent mechanical properties, chemical inertness, and wear-resistance. In addition to the removal rate and surface roughness, subsurface quality is also an important evaluation index that may strongly affect the electronic performance and lifespan of nanodevices [45]. The microstructures of the subsurface beneath the wear track with a depth of ~87 nm produced by a diamond tip under a contact pressure exceeding the plastic yield of GaN material was observed using TEM, and the results are shown in Fig. 6. Given that mechanical removal was dominated by plastic deformation and ploughing over the material yield of the substrate, the diamond tip cannot mechanically remove the GaN surface under the plastic-deformation stage. In a high contact-stress case (plastic-deformation stage), the external mechanical energy from the shear and compressive forces by the diamond tip acted on the sliding contact interface represented as the structural amorphization and lattice distortion (Fig. 6a–c), was also transferred downward the crystal structure of the subsurface layer, thereby damaging it and resulting in many dislocations in the near-contact interface region (Fig. 6b) [46]. These experimental results were similar to the results from computational molecular dynamics simulation on the deformation behavior during abrasive machining of GaN surface against diamond nanoparticle [22,23]. Moreover, the elemental distribution of the cross-sectional map of the scratched track produced by the diamond tip was analyzed by TEM-EDX, and the results are plotted using different colors (Fig. S10 in Supporting Information). The elemental maps showed that no contaminant elements were introduced into the substrate during the mechanical removal process. The above findings indicated that mechanical removal can gain an advantage in the removal efficiency, and mechanochemical removal can obtain the nondestructive substrate/subsurface. Therefore, combining these advantages of mechanical and mechanochemical removal to improve material removal efficiency while reducing substrate/subsurface damage will be a promising research objective of future research on the advanced surface machining of GaN.

3.3. Mechanical-activation effect on mechanochemical-removal processes

Experimental results and analysis indicated that the material removal of GaN surface against Al2O3 microsphere was primarily caused by mechanically stimulated chemical reactions. The static chemical reactions between Al2O3 and GaN can hardly occur with water molecules, suggesting that the chemical activation energy E_a (the magnitude of energy barrier) should be substantially higher than the thermal energy at room temperature [47]. The mechanochemical removal process of GaN substrate against Al2O3 counter-surface, which underwent various activated or transition states (with energy maxima) accompanied by numerous immediate chemical products, was simplified as the chemical coordinate moving from the initial energy state to the final one in the following discussions. With the shearing force of the slid Al2O3 microsphere, E_a could be alternated physically by the external mechanical energy, and the magnitude of reduction in E_a is represented as E_m [48, 49]. Furthermore, the effective activation energy E_{eff} could be expressed as E_{eff} = E_a - E_m [30, 31, 40, 50]. Thus, the normalized mechanochemical removal rate (k) of GaN material through Al2O3 microsphere could be theoretically modeled with a mechanically assisted Arrhenius-type kinetic model [51–55]:

\[
k = A \exp \left( \frac{-(E_m - E_{m0})}{k_B T} \right)
\]

(2)

where k_B is the Boltzmann constant (1.38 × 10^{-23} J/K), A is the pre-exponential factor depending on the unit of the left-hand side of Eq. (2), and T is the temperature at the tribological interface whose change can be negligible due to the ultralow sliding speed during the nanowear process [56]. Based on the dimensionality argument, the mechanical term E_m could be expressed as the applied shear stress times a volume term ΔV*: E_m = σΔV*, where ΔV* is named the critical activation volume describing the difference in the chemical-bond geometry between the equilibrium and transition states strained by shear force during mechanochemical reactions [30,31,50]. For the nanosapphire contact in the present study, the resistive force per unit contact area was assumed to be constant and the real contact area is proportional to the total normal load. Then σ could be estimated by dividing the Atom-onon’s law with the contact area, determining the linear relationship with the Hertzian contact pressure \( P: \sigma = \mu \cdot P + \sigma_0 \), where \( \mu \) is the frictional coefficient of the GaN-Al2O3 sliding interface, and the nonzero pressure-independent term \( \sigma_0 \) may be attributed to the interfacial attractive interaction [57,58]. The average frictional coefficient \( \mu \) was estimated to be approximately 0.12 (Fig. S11 in the Supporting Information). If the \( \sigma \) term was replaced by the above expression, the following equation would be obtained by taking the logarithm of both sides,
3.4. Roles of humidity and sliding speed in mechanochemical removal on GaN surface

The above results demonstrated the mechanochemical removal induced by chemically active Al₂O₃ microsphere under the purely elastic yield and the mechanical removal against a chemically inert diamond tip under plastic yield. To confirm the effect of chemical activity of the counter-surface on the nanoasperity removal on GaN surface, we examined the influences of environmental humidity and processing speed on the removal efficiency of GaN surfaces against Al₂O₃ and diamond tips customized to the practical application of precision machining. Fig. 8a compares the removal volume of wear tracks produced by Al₂O₃ within the ambient humidity range of 3%–80%. The removal volume in the GaN–Al₂O₃ case increased as a function of humidity, but it maintained a constant value within the experimental error in the GaN-diamond case (see Fig. S12a, Supporting Information). The different removal trends under various ambient humidities were primarily due to the counter-chemistry-dependent removal mechanism governing the material-removal behaviors on the GaN surface. As a dominant reactant for the interfacial mechanochemical reaction, water molecules participated in every aspect of the atomic attrition on the GaN substrate, i.e., surface hydroxylation, the formation of interface bonding bridges, and the hydrolysis of chemical bonds of the substrate. However, with the increase in environmental humidity, the effect of stress corrosion on the material removal of GaN surface by using the diamond tip was limited due to the strong corrosion resistance of GaN. Therefore, the single-point mechanical removal dominated by plastic deformation and ploughing effect was independent of humidity.

The effect of processing speed on mechanochemical and mechanical removals of GaN substrate also showed different trends. Fig. 8b displays that with increased sliding speed from 0.1 μm/s to 1000 μm/s, the removed volume of wear tracks produced by the Al₂O₃ microsphere dramatically decreased from 2.6 × 10⁶ nm³ to near zero. However, almost no change in the removal volume occurred by using the diamond tip (as shown in Fig. S12b, Supporting Information) within the speed range of 0.1–100 μm/s, which is different from the significant increase trend observed during the actual macroscopic processing. The highly speed-dependent mechanochemical-removal behavior may be mainly attributed to the dynamic structure and thickness of the adsorbed water meniscus formed at the contacting interface under different speeds [27]. The height/volume of the condensed meniscus logarithmically decreased with the increase in speed or decrease in contact time [59,60]. As described above, the formation of the bonding bridge induced by the dehydration condensation reaction played a vital role in the mechanochemical-removal kinetics. Once the contact time was reduced to the critical value of the meniscus condensation at high speed, the interfacial-bonding bridge hardly formed between the sliding Al₂O₃ tip and the GaN substrate, resulting in a nearly no wear state under the pure elastic contact. These findings may advance the understanding of the mechanism influencing the counter-surface chemistry and mechanical activation in mechanochemical reactions at the GaN–Al₂O₃ interface and provide fundamental knowledge to optimize the ultra-precision surface manufacturing of GaN.
4. Conclusions

The mechanical- and mechanochemical-removal behaviors of the N-faced GaN surface by using diamond and Al₂O₃ nano-asperities were contrastively studied. The mechanical removal induced by plastic deformation and ploughing can be well described by the Archard equation and is independent of environmental humidity and sliding speed. In the Al₂O₃ case, when the contact pressure is far below the plastic yield of GaN material, evident material removal occurs on the GaN surface with the assistance of interfacial mechanochemical reactions. Moreover, the water content and chemically active counter surface are verified to be vital for initiating the mechanochemical reactions, which are positively correlated with the ambient humidity and negatively correlated with the sliding speed. With regard to mechanochemical-removal behavior, Archard law fails to elucidate it, and an exponential dependence of removal rate on contact stress has been found. Analyzing the mechanochemical reactions with the Arrhenius-type kinetic model and Hertzian contact mechanics reveals that the critical activation volume and activation barrier are able to semiquantitatively describe the external mechanical activation for the mechanochemical reactions. All these results provide deep insights into the mechanochemical-removal mechanism of GaN and can serve as a reference for accurately modeling complex material migration in scientific and engineering applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.triboint.2021.107004.

Author statement

Jian Guo: Conceptualization, Writing - Original Draft, Supervision, Funding acquisition. Jian Gao: Investigation, Data Curation. Chen Xiao: Project administration, Conceptualization, Data Curation, Writing - Review & Editing. Gengzhuo Li: Validation, Formal analysis. Hanqiang Wu: Investigation, Data Curation. Lei Chen: Writing - Review & Editing. Linmao Qian: Supervision, Resources. All authors have read and approved the manuscript.

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