The Tribological Properties of Gallium Nitride Under Various Environmental Factors

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The Tribological Properties of Gallium Nitride Under Various Environmental Factors

by

Zhaohua Chang

A Thesis
Presented to the Graduate and Research Committee
of Lehigh University
in Candidacy for the Degree of

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in

Mechanical Engineering

Lehigh University

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Thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science in Mechanical Engineering.

________________________________________
Date Approved

________________________________________
Dr. Brandon Krick, Thesis Director

________________________________________
Dr. D. Gary Harlow, Chairperson of Department
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ABSTRACT

The purpose of this work is to understand the wear mechanisms of III-V nitride semiconductor materials (GaN, AlN) under different environmental conditions such as submerged water, submerged isopropyl alcohol, and ambient air. Previous studies have shown ultra-low wear of GaN with wear rates approaching diamond [1]. Although previous investigations into the influence of sliding speed and humidity have been done, the sliding speeds were relatively low (< 1 m/s) and the influence of water in a fully submerged state has not been done. This work shows that the highest wear rate in submerged IPA is $3.15 \times 10^{-7}$ (mm$^3$/Nm) after 50,000 cycles. The air group has a lowest wear rate of $1.91 \times 10^{-7}$ (mm$^3$/Nm), and the highest one in submerged water is $3.75 \times 10^{-7}$ (mm$^3$/Nm). Under the same load, the wear rate increases as the speed increases. The lowest coefficient friction found in IPA group about 0.1, the air one and water one have a similar coefficient of friction about 0.25. Scanning electron microscopy (SEM) and Raman spectroscopy were used to investigate the effects of shear-induced band bending and changes in chemical composition due to sliding.
Chapter 1

1. Introduction

1.1 Applications of III-V Semiconductors

III-V Nitrides (GaN as well as cubic-BN, AlN, InN, and alloys of these materials) have recently developed significant scientific interest because of their potential applications in high-power, high-temperature microelectronic and optoelectronic devices resistant to radiation damage [2]. Due to these semiconductors having a wide band gap, they have played a crucial part in the commercial production of optoelectronic devices such as green and blue light emitting diodes and laser diodes. Recently, research into these materials has been done to develop ultraviolet light detectors and high-temperature, high-power, and high-frequency microelectronic devices [3-6]. Gallium Nitride is a promising alternative to silicon because it is able to conduct electrons more than 1000 times more efficiently while being able to be manufactured at a lower cost. Additionally, group III nitrides have a low sensitivity to ionizing radiation making it a suitable material for solar cell arrays for satellites. Silicon and silicon oxides are important materials in semiconductor, but silicon itself doesn’t have intrinsic lubrication properties. The silicon’s wear behavior in some extremely high humidity area isn’t good enough. What’s more, because the pollution the rainfall is acidic to some extent, the situation is worse. So, if using the Gallium Nitride work as thin film can protect the device.

1.2 Influence of Environment on Wear

The wear behavior of ceramics is complex and highly dependent on humidity. Water has been shown to reduce wear rates, Tiejun M. et al. observed that 50%SiC DRA forms a hard ‘mechanically alloyed' surface layer comprised of a high volume fraction of SiC particles that
causes a significant reduction in wear. For silicon nitride, Ishigaki et al. have shown that absorbed water enhances the plastic flow of the material resulting in a reduction of wear rate and friction coefficient. Anna L. et al. found the alcohol vapor prevented the wear of and alkoxide termination of the surfaces raises the energy barrier required to cleave the adjacent Si-O-Si bonds upon the reaction of the surface Si atom with impinging vapor molecules as compared to hydroxide terminated surfaces.

Water not only affects the wear performance of ceramics, but chemical changes have also been shown to occur when ceramics are used in water-lubricated applications. The GaN surface preparation techniques must also be investigated to provide atomically smooth, damage-free surfaces, such as chemical mechanical polishing (CMP). CMP uses a combination of chemical and mechanical reactions to remove material leaving a planarized, damage-free surface. Ideally, material removal is achieved by chemically altering the surface to a mechanically weaker form; this material is then abraded from the surface leaving the bulk undisturbed. Shear induced chemical reactions (tribochemistry) of h-BN nanoparticles in tribological mechanisms have been shown to generate $H_3BO_3$ and $B_2O_3$ when sliding in water.

Although significant work has been done on investigating the impact of the environment on ceramics, GaN has only recently been studied for use as a tribological material. Little work has been done on the wear and friction of GaN. Zeng et al. investigated the friction and wear performance of GaN under varying humidity and found that wear rate is directly affected by humidity, with the wear rate ranging from $9 \times 10^{-9} \text{mm}^3/\text{N} \cdot \text{m}$ in dry nitrogen to $9.5 \times 10^{-7} \text{mm}^3/\text{N} \cdot \text{m}$ under humid air.

### 1.3 Wear of GaN

GaN has shown ultralow wear rates approaching that of the diamond when in a dry nitrogen environment. While the bulk of the research on GaN has been done looking at
electronic properties for applications to semiconductors, very little work has been done to investigate the tribological properties. Zeng et al. found that the wear rate of GaN is dependent on the crystallographic sliding direction and showed that there is a 60° periodicity of wear rate and coefficient of friction. Though the highest friction coefficient occurs on the $<1\bar{1}00>$ plane, this plane has the lowest wear rate with a value of $6 \times 10^{-8}$ mm$^3$/Nm. The highest wear rate occurs when sliding on the $<1\bar{2}10>$ plane with a value of $1.4 \times 10^{-7}$ mm$^3$/Nm yet the coefficient of friction is the lowest. Using molecular static simulations and calculated the energy between atoms, the authors attributed the difference in wear rates to the higher energy barrier found along $<0\bar{1}00>$, resulting in a more difficult removal of the material.[12]

*Figure 1 Wear Rate of Different Materials [7]*
1.4 Shear-Induced Band Bending

The authors additionally found that sliding on the GaN surface causes permanent changes to the band structure. Inside the wear track, shear induced deformation of the material causes band bending by more than 0.5eV. The combination of shear and contact stresses produce newly formed materials, causing spatially variant band bending. This process of shear-induced modification to the band states has been given the term ‘tribodoping’. [13]

![shear-induced, spatially variant band bending (BB) of GaN](image)

**Figure 2 Band Bending of GaN[7]**

1.5 Research Objective and Hypothesis

1.5.1 Question:

The goal of this work is to answer the question, how does the sliding fluid, such as water and isopropyl alcohol, affect the wear rate and shear induced band bending of GaN. Past work has investigated the impact of humidity, sliding duration, sliding speed and normal load on band bending yet submerged environments are still unknown.
1.5.2 Hypothesis

It is hypothesized that the sliding GaN submerged in water would have the highest wear rate because water can cause the GaN to oxidize. This is in line with the previously discovered increase in wear rate with increasing humidity. The IPA is expected to act as a weak boundary lubricant and reduce friction and wear. However, the possible effects of tribochemistry are unknown and can be beneficial or detrimental depending on the chemistry occurring between the solid surface and fluid.[14] Beneficial chemistry can enhance the effectiveness of a lubrication method. Detrimental chemistry facilitates the formation of wear debris particles which can accelerate wear. Assuming a chemical mechanism in which the adsorbed molecules react with the surface and the surface species formed via these reactions alter the energy barrier to break the GaN bond at the substrate surface.
Chapter 2

2. Experiment

2.1 Materials

Gallium Nitride samples (~3um thick) are grown on 2-inch single crystal sapphire wafers by metal-organic chemical vapor deposition (MOCVD). MOCVD is a well-known, controllable synthesis method. It features in the all vapor phase reaction, which allows the control of precursor ratio, growth time, and growth rate. It also features in the capability of low-temperature growth.

[15] The counter samples used are single crystal ruby balls (ruby, Swiss Jewel, Grade 25, 1.5mm diameter). All samples were cleaned by sonicking them for 5 minutes in acetone, IPA and DI water.

Table 1 Material Properties and Working Conditions [15,16]

<table>
<thead>
<tr>
<th>Material Property</th>
<th>GaN</th>
<th>Ruby ball</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus</td>
<td>290 GPa</td>
<td>350 GPa</td>
<td>Sliding speed</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.25</td>
<td>0.25–0.3</td>
<td>Normal load</td>
</tr>
<tr>
<td>Hardness</td>
<td>16 GPa</td>
<td>22 GPa</td>
<td>500mN</td>
</tr>
</tbody>
</table>

2.2 Methods

2.2.1 Linear Reciprocating Tribometer

All tests were performed in a ball-on-flat configuration using a custom bidirectional reciprocating multi station tribometer that can test up to four samples simultaneously. Samples can be mounted and exposed to air or fluid cells can be mounted for submersion into liquids such
as water. Linear motion is provided by using a stepper motor (TSM-23Q-2AG) to drive a linear ball screw stage with a sliding velocity of 5 mm/s. Load control was accomplished by using four individual positioning stages, each controlled by a NEMA 11 stepper motor. Data acquisition was done using a Teensy 3.5 and custom MATLAB software. The tribometer is in a custom nitrogen box for environmental control and can be exposed to ambient air or dry nitrogen which allows for testing in various environments. Ruby balls are mounted to a 4-40 set screw by super gluing them, then mounted to the cantilever and locked in place with a lock nut.

Before any experiment, the surfaces of the ruby balls were imaged using a scanning white light interferometer (SWLI) to ensure no debris or glue on the surface. All tests were performed at a normal force of 500 mN (hertzian contact pressure of 2GPa). This load was chosen to match previous experiments and to help reduce the amount of sliding cycles needed to obtain a wear rate. The contact pressure falls below the plastic deformation threshold of GaN which is approximately 10 to 11 GPa. [17] The material properties and test condition are in Table 1.
Figure 3 Multi Mini DAQ
2.2.2 High Speed Rotary Tribometer

The high speed rotary tribometer is a pin-on-disk tribometer, was built on high loads and high speed for bulk-on-disk to test metals called rotatry reciprocating tribometer. There are two different direction micrometers on the cantilever, one is used to control the direction, and the other one is controlling the distance. The spin stage is connected to a motor by belt. Data acquisition was done using a custom MATLAB software. Matlab was used to simultaneously display the normal force and friction.

The next step is to verify the probe screws on the cantilever was concentric on the sample holder and find the relationship between the number of grids and the radius of the experimental
samples. Using a 2-inch aluminum on the sample holder, five pre-tests were operated with the
grid number of 5,10,15,20,25 separately. SWLI was used to measure radius of each wear track,
and to deduct a linear relationship between the micrometer grids and the sample radius.

To calibrate the normal forces and friction forces, two sensors were adopted to read
experimental data, which were connected with the load cells. The method was implemented to let
the load cell hang on several weights, such as 0.1, 0.5 and 1N, then recorded the data of normal
forces on the Matlab, by finding the linear relationship to get the fraction number of normal
forces and friction forces.

Table 2 Radius Calibration

<table>
<thead>
<tr>
<th>Stage R Micrometer on tribometer</th>
<th>R SWLI Right (mm)</th>
<th>R SWLI Left (mm)</th>
<th>Fit (mm)</th>
<th>Fitting Thing</th>
<th>Fmeas/Fact</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20.13</td>
<td>-20.13</td>
<td>20.13</td>
<td>3.96E-03</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>15.13</td>
<td>-15.14</td>
<td>15.14</td>
<td>7.14E-03</td>
<td>1.00</td>
</tr>
<tr>
<td>15</td>
<td>10.16</td>
<td>-10.16</td>
<td>10.14</td>
<td>-0.02</td>
<td>1.00</td>
</tr>
<tr>
<td>20</td>
<td>5.16</td>
<td>-5.18</td>
<td>5.16</td>
<td>4.3E-03</td>
<td>0.99</td>
</tr>
<tr>
<td>25</td>
<td>0.66</td>
<td>-0.66</td>
<td>0.66</td>
<td>6.79E-06</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 5 Radius Calibration

Figure 6 Solidworks of High Speed Tribometer
Vibrations increase with speed which increases a chance of ruby ball to detach, therefore, a ball holder is used.

![Ball Holder](image1)

**Figure 7 Ball Holder**

![High Speed Tribometer](image2)

**Figure 8 Costumed High Speed Tribometer**

High speed tests were performed using parameters in the Table 3, each set was repeated three times. At higher speed, velocities had to be slightly adjusted to avoid hitting harmonic
frequency and the subsequent vibration. The range of adjustment was kept within 15-20% of the target linear speed.

Table 3 Experimental Parameters

<table>
<thead>
<tr>
<th>Normal force</th>
<th>Linear speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4N</td>
<td>0.1m/s</td>
</tr>
<tr>
<td>1N</td>
<td>2.8~3.25m/s</td>
</tr>
<tr>
<td>2N</td>
<td>4.25m/s~5m/s</td>
</tr>
</tbody>
</table>

2.2.3 Wear Measurement

Surface topography was measured by imaging the wear scars using a scanning white light interferometer (SWLI; Bruker Contour GT-K) 3D scans. Area of the wear scar cross section was calculated by leveling 2D cross sections of the wear scar (linear subtraction) and numerically integrating the area of the wear scar below zero. To calculate the specific wear rate (K), Archard’s formula which relates total volume lost V (volume worn in mm³) per applied force Fn (applied normal load in N) over a sliding distance d (sliding distance in m) was used. Equation 1 is the formula for a specific wear rate:

\[
K \left[ \frac{mm^3}{Nm} \right] = \frac{V[mm^3]}{F_n[N] \times d[m]} \tag{1}
\]

The Archard wear rate from the linear reciprocating tribometer can be calculated from experimentally measured cross-sectional areas by equation (2)

\[
K \left[ \frac{mm^3}{Nm} \right] = \frac{A \times L}{F_n \times 2 \times N \times L} \tag{2}
\]

In this equation, \(F_n\) is the normal force (in N), \(N\) is the number of reciprocated cycles (two sliding passes per cycles), \(L\) is the length of the wear scar, and \(A\) is the average area of cross-
sectional scans from profilometry measurements (in mm³) [18]. Note the units of length are mm in the numerator and m in the denominator; a more convenient calculation of wear is:

\[
K \left[ \frac{\text{mm}^3}{\text{Nm}} \right] = \frac{A}{F_n \times 2 \times N \times 1000}
\]

Wear experiments were performed using a stripe test which is a series of experiments where the track length is shortened to allow for multiple regions with different amounts of sliding cycles. Tests were done by sliding 1k cycles at 4 mm, 10k cycles at 3 mm, 25k cycles at 2 mm and 50k cycles at 1 mm. Wear rate measurements were then taken in each section.

3D profile (250 μm * 320 μm) is taken for each segment, 10 linescan per segment. Wear rate is based on the average worn area of the scans in the segment, standard deviation shown as error bars.

For rotary pin on disk experiments, an automated rotary wear scar measurement was built for the profilometer. An arduino/Matlab custom code moved a precision rotary piezo stepper
stage (PI M 660.55) in precise increments and called the profilometer to acquire a scan. This enabled very high throughput acquisition of topographies of the wear scar as a function of theta (see fig. 10). For the high speed experiment sample, there is 810 scans per sample, 90 3D scans per wear track, 10 linenscan per scan.

![3D wear scan](image1)

Figure 10 Rotary Piezo Stepper

### 2.2.4 Friction Coefficient

A friction loop consisted of a forward stroke and a reverse stroke. For each reciprocating cycle, the friction coefficient was calculated by averaging the middle 20% of the friction loop.[11] While variation in the data is apparent, not all the scatter can be attributed to the apparatus-based uncertainty described here. In fact, a significant source of variation in these measurements is a large number of factors that influence friction and the difficulty in controlling all of these variables. For example, it is impossible to use exactly the same GaN sample for all tests because it is destroyed during testing.
Figure 11 Example of Friction Loop
Chapter 3

3. Results and Discussion

3.1 Friction coefficient

A representative trend of the friction coefficient over the entirety of a test is shown in fig. 12. For all three cases, the friction coefficients are very similar and match with values measured by Zeng et al. The samples ran submerged under IPA always have slightly lower friction than air or submerged water, likely due to the lubricious behavior of IPA. Around 25k cycles, there is a drop in the friction coefficient which is likely a wear event which possibly shrinks the contact area. Interestingly, the initial friction coefficient in air is initially lower than water. This might be due to some initial surface oxides that wear away.
Noise in the data is filtered out using averaging. The noise most likely electrical and some can still be seen in fig. 13 as little spikes and dips in friction coefficient. To ensure that changes in friction coefficient are due to load variation, plot the normal force over the entire test. For all three cases, normal load only varied by a few percents. For air, there is a slight increase in the normal load of about 4mN, which is most likely electrical drift or slight movement in the motor could simply be controlling the force. The jump seen around 25k cycles in fig. 13 is attributed to restarting the experiment at a slightly different load but is still not very impactful because it is only 2% of the entire load. The load for the tests in water and IPA are 6% below the target but is very consistent throughout the experiment. Again, electrical noise is seen in all three experiments as load spikes, with the greatest spike being ~4% of the load which is well within error tolerances.
3.2 Wear Rate

3.2.1 Wear Rate at Different Environment

Wear rates for IPA, water and air at 10k, 25k and 50k cycles are shown in fig. 14. For IPA and water, the values are very similar yet in the air the wear rate drops by a factor of 3 or more. Additionally, fig. 14 shows that as sliding cycles are increased the wear rate slowly increases by a factor of 7.
Figure 14 Wear Rate of All Conditions Up To 50k Cycles in Test 1

Data point is average of 10 line scans, error bars are standard deviations.

The wear rate of the tests under different environments and calculated at various sliding intervals are in the table below.

Table 4 Wear Rate at Different Conditions

<table>
<thead>
<tr>
<th>condition</th>
<th>wear rate (mm$^3$/Nm)</th>
<th>cycles</th>
<th>TEST</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN in water</td>
<td>2.77E-07</td>
<td>10,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.57E-07</td>
<td>25,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.85E-07</td>
<td>50,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in water</td>
<td>3.44E-07</td>
<td>10,000</td>
<td>2</td>
</tr>
<tr>
<td>GaN in water</td>
<td>3.75E-07</td>
<td>25,000</td>
<td>2</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.15E-07</td>
<td>50,000</td>
<td>2</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.46E-07</td>
<td>10,000</td>
<td>3</td>
</tr>
<tr>
<td>GaN in water</td>
<td>3.04E-07</td>
<td>25,000</td>
<td>3</td>
</tr>
<tr>
<td>Material</td>
<td>Wear Rate</td>
<td>Wear Life</td>
<td>Wear Rate Category</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>--------------------</td>
</tr>
<tr>
<td>GaN in water</td>
<td>3.29E-07</td>
<td>50,000</td>
<td>3</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.85E-07</td>
<td>10,000</td>
<td>4</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.49E-07</td>
<td>25,000</td>
<td>4</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.72E-07</td>
<td>50,000</td>
<td>4</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.20E-07</td>
<td>10,000</td>
<td>5</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.27E-07</td>
<td>25,000</td>
<td>5</td>
</tr>
<tr>
<td>GaN in water</td>
<td>2.58E-07</td>
<td>50,000</td>
<td>5</td>
</tr>
<tr>
<td>GaN in IPA</td>
<td>3.34E-07</td>
<td>10,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in IPA</td>
<td>3.45E-07</td>
<td>25,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in IPA</td>
<td>3.12E-07</td>
<td>50,000</td>
<td>1</td>
</tr>
<tr>
<td>GaN in IPA</td>
<td>5.62E-07</td>
<td>10,000</td>
<td>2</td>
</tr>
<tr>
<td>GaN in IPA</td>
<td>4.26E-07</td>
<td>25,000</td>
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<td>GaN in IPA</td>
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<tr>
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<td>1.91E-07</td>
<td>50,000</td>
<td>2</td>
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<tr>
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<td>GaN in air</td>
<td>3.57E-07</td>
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<td>5</td>
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<td>GaN in IPA vapor</td>
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<td>GaN in IPA vapor</td>
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<td>50,000</td>
<td>1</td>
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</table>

The overall wear rate of GaN submerged water is 2.74E-07 (\text{mm}^3/\text{Nm}) after 10k sliding cycles, 2.82E-07 (\text{mm}^3/\text{Nm}) after 25k sliding cycles, 2.72E-07 (\text{mm}^3/\text{Nm}) after 50k sliding cycles.
cycles. The overall wear rate of GaN submerged IPA is $2.86E-07 (\text{mm}^3/\text{Nm})$ after 10k cycles, $2.49E-07 (\text{mm}^3/\text{Nm})$ after 25k sliding cycles, $2.37E-07 (\text{mm}^3/\text{Nm})$ after 50k sliding cycles. The overall wear rate of lower humidity air is $1.45E-07 (\text{mm}^3/\text{Nm})$ after 25k sliding cycles. The wear rate of IPA vapor is $7.37E-08 (\text{mm}^3/\text{Nm})$ after 25k sliding cycles, $2.35E-07 (\text{mm}^3/\text{Nm})$ after 50k sliding cycles. The groups 4,5,6 ran at high humidity of about 70%. It was hypothesized the air group has almost the same wear rate as in the water group, however, air is lower at low number of sliding cycles. At 50k cycles, wear was comparable for air and water. From the each group’s wear rate, the IPA has a similar wear rate as water one. Test 4 has a different wear rate for IPA at 25000 cycles which is closed to the IPA vapor. This might be caused by the IPA evaporation at some time before the experiment ended.

3.2.2 Wear Rate at High Speed

The high speed tests ran 200,000 cycles per group. The result above shows the different group of the high speed experiment has a different wear rate, it seems like sample 2 has a better result. But from the result of friction of coefficient the test1, it shows the result was much more stable. In different experimental groups, different 2-inch GaN wafer samples were used, so the quality could be another factor which would influence the result. So, the sample used in experiments might have better quality, which can be used to explain the why sample 2 had a better wear rate but higher coefficient friction. Within the group of the same load, with the speed increased, the wear rate also increased. Within the group at the same range of speed, the wear rate increased with the normal force increased. The only different result is at the load of 2N and sliding speed 5m/s within group 1, which may be caused by the vibration. The width of this wear track changed a lot. Also, the test at the load of 2N and sliding speed 3.25m/s had a huge jump between 50 degrees and 100 degrees, which increased the wear rate. Both factors can cause the error.
### Table 5 Wear Rate of High Speed

<table>
<thead>
<tr>
<th>condition</th>
<th>Wear rate (mm$^3$/Nm)</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N 0.1 m/s</td>
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<td>1</td>
</tr>
<tr>
<td>2N 0.1 m/s</td>
<td>2.59E-08</td>
<td>2</td>
</tr>
<tr>
<td>2N 0.1 m/s</td>
<td>7.18E-08</td>
<td>3</td>
</tr>
<tr>
<td>2N 3.25 m/s</td>
<td>4.54E-07</td>
<td>1</td>
</tr>
<tr>
<td>2N 3.25 m/s</td>
<td>2.72E-07</td>
<td>2</td>
</tr>
<tr>
<td>2N 3.25 m/s</td>
<td>4.33E-07</td>
<td>3</td>
</tr>
<tr>
<td>2N 5 m/s</td>
<td>2.16E-07</td>
<td>1</td>
</tr>
<tr>
<td>2N 5 m/s</td>
<td>2.82E-06</td>
<td>2</td>
</tr>
<tr>
<td>1N 0.1 m/s</td>
<td>8.14E-08</td>
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</tr>
<tr>
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<td>3.83E-08</td>
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<td>1N 0.1 m/s</td>
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</tr>
<tr>
<td>1N 3.25 m/s</td>
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<td>1</td>
</tr>
<tr>
<td>1N 3.25 m/s</td>
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<td>2</td>
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<td>1N 3.25 m/s</td>
<td>1.43E-07</td>
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<td>3.20E-07</td>
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<tr>
<td>1N 4.25 m/s</td>
<td>7.49E-08</td>
<td>3</td>
</tr>
<tr>
<td>0.4N 0.1 m/s</td>
<td>3.47E-08</td>
<td>1</td>
</tr>
<tr>
<td>0.4N 0.1 m/s</td>
<td>2.17E-08</td>
<td>2</td>
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<tr>
<td>0.4N 0.1 m/s</td>
<td>7.57E-08</td>
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<tr>
<td>0.4N 2.8 m/s</td>
<td>4.62E-08</td>
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<tr>
<td>0.4N 2.8 m/s</td>
<td>2.03E-08</td>
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<td>0.4N 2.8 m/s</td>
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<td>0.4N 4.25 m/s</td>
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<tr>
<td>0.4N 4.25 m/s</td>
<td>6.24E-08</td>
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</table>
Figure 15 Wear Rate at 2N, 5m/s, Sample 1

Figure 16 Wear Rate at 2N, 3.25m/s, Sample 1
Figure 17 Wear Rate at 2N 0.1m/s, Sample 1

Figure 18 Wear Rate at 1N 0.1m/s, Sample 1
Figure 19 Wear Rate at 1N, 3.25m/s, Sample 1

Figure 20 Wear Rate at 1N, 4.25m/s, Sample 1
Figure 21 Wear Rate at 0.4N 0.1m/s, Sample 1

Figure 22 Wear Rate at 0.4N 2.8m/s, Sample 1
Most of those wear rates of 360 degrees figure had a jump point at (50~150 degrees), which may be accounted by the vibration that was caused by the sample surface was not even.
Figure 24 Tribology Summary for High Speed Test, Lab Air about 25% RH
3.3 Third Bodies

The experiments at high speed (load of 2N and speed 0.1 m/s) showed high vibration. It isn’t caused by the harmonic frequency, because at this normal force and speed there isn’t such high vibration. Every time it happened after 8~10 hours, so there must be another reason. To investigate this phenomenon, the surface of GaN was blown off after every test to get rid of the accumulated war debris. Interestingly, the repeated tests showed lower vibration. The following figure shows the influence of wear debris.
3.4 Compare wear rates and wear scars

Fig. 26,27,28,29 show 2D representative line scans for each condition used by SWLI and Matlab. After each experiment, samples were cleaned with acetone, IPA and DI water to remove any wear debris before imaging.
Comparing the linescan at IPA vapor and air, after 50,000 sliding tests, the wear track under IPA vapor is deeper since the two wear track had a similar width. It shows the IPA vapor
group has a higher wear rate, the calculated wear rate confirms this. So, the IPA vapor has higher the wear rate.

Figure 28 Wear Linescan and Wear Track Submerged in IPA
It’s obvious that the group in submerged water and in submerged IPA has a higher wear rate than the air and IPA vapor group, because these two groups have a wear scar after 10,000 sliding tests. From the linescan, the wear track of in submerged IPA and in submerged water after 10,000 cycles has a similar depth as the wear track in air and IPA vapor after 25,000 cycles. Also the last two groups have a higher wear rate. Between these two groups, the image and linescan of wear track is alike, from the calculated wear rate, their wear rates are almost the same. So the IPA and water both increase the wear of GaN, and that’s why the IPA vapor group has a higher wear rate than air. The IPA vapor group has a lower wear rate than in submerged IPA one, because the IPA concentration is lower.
3.5 Surface analysis

3.5.1 Secondary electron mode

SEM measurements (SEM, ZEISS 1550) were utilized to image the morphology of the worn surfaces for comparing the wear modes under different conditions. The inhomogeneity of the surface states was visualized and confirmed with low voltage scanning electron microscopy (LVSEM). Because upward band bending will build up an electrical field pointing from the bulk to the surface, LVSEM can be used to indirectly measure the amount of band bending on the surface.[14] Each scanned track using 4 different accelerating voltages, 0.5kV, 2kV, 5kV, 10kV. The inlens detector was used at working distances between 3~8mm.

Fig. 30 shows the SEM images over the various accelerating voltages for the water and IPA samples. Looking at the sample submerged in water, at 0.5kV the wear scar is very dark, indicating a significant amount of band bending. As the voltage is increased to 10kV, all the dark regions disappear. Interestingly, the IPA track at 0.5kV has significantly fewer dark regions then the water track. This points to less band bending when submerged in IPA. At 5kV there are no dark regions in the IPA track, while the water sample has a few dark streaks. This result shows that water increases the amount of band bending from sliding and IPA reduces it. This could possibly be due to the lubricious behavior of IPA reducing the shear stress on the surface. As fig. 12 shows, the friction coefficient in IPA is ~30% lower than in water which means the shear stress on the surface is 30% lower in IPA. If there is less stress to modify the surface it would make sense that there is less band bending when running in IPA than water. CMP uses a combination of chemical and mechanical reactions to remove material leaving a planarized, damage-free surface.[19] Ideally, material removal is achieved by chemically altering the surface
to a mechanically weaker form. If the chemical mechanical polishing of GaN under IPA fluid may have a better bulk GaN quality than under water.
Figure 30 Low Voltage SEM of GaN Wear Scar in Water (left) and IPA (right). Transition from Dark to Light indicates Band Bending as A Function of Acceleration Voltage.
Figure 31 SEM of Wear Scars for High Speed (0.1, 3 and 5 m/s) at Various Normal Loads (0.4, 1 and 2 N)

Figure 32 SEM of Wear Scars for High Speed Test Indicates Abrasive Wear
From the result of SEM of the high speed group, the band bending while the sliding speed increasing, and increase the normal load, band bending still goes up. Abrasive wear founded on the wear track, but it only exists in the 2N group in 3m/s and 5m/s group. At high load and high speed condition, there was abrasive wear, that may cause by the higher vibration.

### 3.5.2 Raman Spectroscopy

In order to investigate chemical changes to the surface, Raman spectroscopy was performed on the three different samples. A Raman spectrum measures the inelastic scattering of photons. The loss of photon energy which occurs during Raman scattering is transferred into greater vibrational or rotational energies of a molecule [20,21]. This method can provide rich information about the molecular structure of the sample and specifically species on the surface.[22] By analyzing peak positions in each spectrum and the relative intensities, changes in the chemical composition of the material can be observed. Each sample was measured inside the wear track to observe changes due to sliding, and a reference was taken outside the track. Fig. 33 show representative Raman spectra with peak and intensity labels for the wear scars and references for the three different cases.
The Raman Spectrum result for the sample is shown in Fig. 32. In order to analyze the effects of sliding the chemical changes of GaN, it is crucial to understand the Raman spectra of pure GaN. GaN has a hexagonal wurtzite structure and belongs to the $C_{6h}$ symmetry group. group theory predicts two $A_1$, two $B_1$, two $E_1$, two $E_2$ modes ($A_1, E_1, E_2$ are Raman active).

### Table 6 Intensity of Raman Peaks Normalized to GaN(547 cm$^{-1}$) Peak Intensity

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$Ga_2O_3/GaN$</th>
<th>$A_1(g)/GaN$</th>
<th>$A_1(Lo)/GaN$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wear track in air</td>
<td>0.70</td>
<td>0.07</td>
<td>0.53</td>
</tr>
<tr>
<td>Wear track in Submerged IPA</td>
<td>0.74</td>
<td>0.09</td>
<td>0.49</td>
</tr>
<tr>
<td>Wear track in Submerged Water</td>
<td>0.19</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>GaN sample in air</td>
<td>0.57</td>
<td>0.07</td>
<td>0.48</td>
</tr>
<tr>
<td>GaN sample in Submerged IPA</td>
<td>0.70</td>
<td>0.07</td>
<td>0.54</td>
</tr>
<tr>
<td>GaN sample in Submerged Water</td>
<td>0.13</td>
<td>0.02</td>
<td>0.10</td>
</tr>
</tbody>
</table>

In our result of Raman spectra, the GaN in $A_1$ mode appears at 547 cm$^{-1}$, and from the reference, the number is in a range from 531~534(Ref.23~26). This spectra agree very well with literature, indicating that our GaN is indeed GaN. As excepted from the Raman selection rules for the wurtzite structure, the $A_1$ (LO) phonon mode is found near 729 cm$^{-1}$. The peak at 426 cm$^{-1}$ is the sapphire substrate ($A_{1g}$) mode of sapphire respectively.[27]
Because the test was in environments with water, oxides are of particular interest because oxides can be good wear and friction modifiers. If formed gallium oxide (Ga$_2$O$_3$) on the surface, Raman should be able to identify this. There is literature using Raman spectroscopy to characterize Ga$_2$O$_3$ [28-29]. The measured peak for this spectra is 395 $cm^{-1}$, reference the work from other people, their peaks are at the range of 387~409 (Ref.30, 31).

Comparing the ratio of each peak in the wear track, the IPA group has the highest Ga$_2$O$_3$ ratio about 0.74, but the sample used for this test has a different quality. The water and IPA group increase the similar ratio of Ga$_2$O$_3$, the air one increases more. During the sliding tests, water and IPA may help to generate Ga$_2$O$_3$ which lead to a higher ratio on the sample surface.

### 3.6 Impacts

Like many tribological experiments involving wear, the nature of the wear behavior can always be linked to the influence of water. For GaN, this holds true and that water in all three cases is the main reason for the wear behavior. When exposed to water, be it submerged, in air or in solution in IPA, water and GaN are competing between tribochemical oxidation of the surface and the removal of surface oxides/hydroxides. Fig.34 illustrates the tribochemical oxidation and wear of GaN when exposed to humid environments. When submerged in water, the oxidation rate is faster resulting in a thicker average oxide layer which in turn has a higher wear rate and is removed faster. For IPA, alcohols absorb water very easily which results in a similar behavior of a surface oxide developing and getting worn away. The benefit of IPA is that it lowers the friction coefficient because of the lubricious nature of alcohols. In air, the amount of water is drastically less than when in water or IPA and the oxide layers form slower. The slower rate of formation results in lower wear which agrees well with our data. Even in air and water, the friction coefficient remains low because water also acts as a lubricant, though not as well as IPA. The influence of pH remains open, it is hard to attribute the lower pH of IPA to any significant
influence on wear rate because the wear rates for IPA and water are very close. From the previous work, the tribological properties of GaN under varying humidity has been known. This work is fulfilling the relationship between GaN’s tribological properties and various environmental factors. The wear resistance of GaN approaches that of diamonds and promises to open up applications in touch screens, space vehicles and radio-frequency microelectromechanical systems (RF MEMS), all of which require high-speed, high-vibration technology.[32] At this work, the wear behavior under high speed and high load has been investigated. Surface preparation techniques must also be investigated to provide atomically smooth, damage-free surfaces, such as chemical mechanical polishing. During the CMP process, the friction coefficient can influence the material removal rate. As increasing the material removal rate, it will be helpful to increase the productivity in industrial.

Figure 34 Illustration of Wear Mechanism of GaN Under Water
3.7 Future work

In future work, to have a better result, it’s better to set the experiment under IPA vapor, which can reduce the influence of evaporation. For future experiments, GaN should be tested in media of various pH such as acids or alkalines to further investigate the influence of pH on wear behavior. Additionally, the influence of temperature on friction and wear would be a very interesting study. Further exploration of the surface chemistries of GaN would be useful in further understand the formation of surface oxides and hydroxides as the current data is only very preliminary.
4. Conclusion

Tribological properties of GaN were evaluated with different loads, speed and environments.

1. The wear rate of GaN increases as the load increases.
2. The wear rate of GaN increases as the speed increases.
3. The wear debris causes a high vibration which leads to more errors on wear rates.
4. The wear rates of GaN submerged IPA and water are similar.
5. The IPA wear track has less band bending than the water one. Higher load has more band bending, higher speed has more band bending.

For future experiments, the influence of pH and temperature on wear behavior and friction would be a very interesting study.
Bibliography


Biography

Zhaohua Chang received the B.Eng. degree in mechanical engineering from Hefei University of Technology, Anhui, China, in 2017. He is currently doing research with Professor Brandon A. Krick and working toward the M.S. degree within the Department of Mechanical Engineering and Mechanics, Lehigh University.