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MOLECULARLY THIN RHEOLOGICAL AND CONTACT INTERFACES

BY

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THESIS

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Urbana, Illinois

Adviser:

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ABSTRACT

A molecularly thin lubricant layer (of the order of 1-2 nanometers thick) has been shown to provide bearing forces at the interface between contacting solid surfaces under light loads and high shear rates. This phenomenon is important, for example, in the head-disk contact in magnetic storage hard disk drives to ensure that some of the contact is sustained by the lubricant layer and thus avoiding damage of the solid surfaces. The magnitude of the normal and tangential bearing forces that the lubricant layer can provide depends on temperature, viscosity of the lubricant, sliding velocity and radius of gyration of the lubricant molecules. This study shows that viscosity has the greatest effect on the load bearing capacity of the molecularly thin lubricant. Thus, by controlling the flash temperature and the ratio of molecularly thin lubricant-to-bulk viscosity, the bearing load carrying capacity of the layer can be controlled. This would allow for the contact to be sustained within the mobile lubricant layer, avoiding solid contact so as to protect the diamond-like carbon coating, and thus reduce wear and potential catastrophic failures.

Another part of the thesis is the work on nano-tribological behavior of Hafnium-Diboride thin films. Dense, hard nanocrystalline films of HfBN and multilayer ones of HfB$_2$/HfBN compositions having thickness in the range of 100-600 nm were deposited using chemical vapor deposition (CVD) technique. The roughness values of HfBN film is extremely small, with a value of 5.38-7.63 nm so it is compatible for use as a very smooth surface such as in microscale miniature systems. Nano-indentation and nano-scratch experiments were done to investigate friction and wear behavior of the films. HfBN exhibited lower coefficient of friction (COF) compared to the multilayer HfB$_2$/HfBN. The amorphous as-deposited films were subjected to
annealing at 700 °C in order to study their mechanical properties in the post-treatment conditions. In comparison to as-deposited films the annealed films possessed lower COF (COF 0.02 lower). The overall response of the annealed HfBN is outstanding making it compatible for wear resistant, very low roughness coating.
To my family
ACKNOWLEDGEMENT

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CHAPTER 1

Introduction

The hard-disk-drive storage device for computers now a days have very thin layer of lubricant to ensure high storage capacity. Whereas Hafnium Boride thin films are coating materials which can withstand high temperature and possess good tribological properties. These two phenomenon are studied in this thesis work.

1.1 Molecularly thin lubricant for hard-disk drives

It is important to bring the read/write elements of the recording head at a Head Disk Interface (HDI) of a hard disk-drive (HDD) as close as possible to the disk surface to achieve the highest possible recording density. For a recording density of 1 Tbit/in$^2$, the magnetic clearance (the distance between the read/write elements and the disk magnetic layer) must be reduced to below 6.5 nm [1]. One of the main engineering barriers in attaining Tbit/in$^2$ areal densities lies in the area of interfaces, specifically achieving the necessary physical clearance between the slider and disk surfaces [2]. To increase the operational life of HDDs, it is important to avoid contact between the slider and disk surface. Contact recording, with the slider physically approaching and dragging on the disk surface during operation, could yield the minimum practical clearance. However, contacting the disk surface is not desirable as it results in vibrations and wear; research also indicated that due to high interfacial adhesion combined with a shock event can also lead to slider/head crashes [3]. Thermal fly-height control (TFC) technology was introduced to avoid dynamic instabilities observed with sub-5-nm clearances. TFC uses a thermal element to create a protrusion or bulge around the read/write elements of the slider and bring them close to the rotating disk surface, while the slider body remains flying nominally at about 10 nm [4].
To minimize wear of the slider and disk due to contact and also to protect against corrosion, a very thin layer (~1-1.5 nm) of perfluoropolyether (PFPE) lubricant is used over the Diamond-Like Carbon (DLC) coating. Customarily, molecularly thin lubricant (MTL) contact has been neglected in rough surface contact and sliding models [5] by assuming that the lubricant is readily displaced upon slider-disk contact. A rough surface model of MTL contact was proposed by Vakis and Polycarpou [6], where the model builds on a single asperity model [7] that accounts for dynamic shearing experiments with polymeric thin lubricants [8, 9], and is coupled with an existing rough surface dynamic contact model with friction [9, 10]. The MTL model has also been extended to include variable lubricant surface energy [11, 12].

Cho et al. performed experiments which proved that the MTL viscosity is different from that of the bulk viscosity [13]. To quantify these differences between bulk and thin-film viscosity, they developed an instrument to measure the shear of parallel single crystal solids separated by molecularly-thin lubricant films. The effective shear viscosity is enhanced compared to the bulk, relaxation times are prolonged and nonlinear responses set in at lower shear rates. From another experimental investigation it has been reported that exceptionally low energy dissipation is possible when fluids move past solid surfaces that are sufficiently smooth [14]. Molecular dynamics (MD) simulations have shown that wall interaction and molecular end-group functionality affect the behavior of the lubricant layer, while lubricant confinement (separation between the solid surfaces) and shear rate were found to play a critical role in determining the lubricant’s liquid- or solid-like responses [15, 16]. Furthermore, MD simulations have shown that there is a transition that tends to nucleate in distorted or imperfect regions in the lubrication film [17], which they term as squeeze-out region. This transition is due to molecular layering: When the contact is at a single molecular layer, then the squeeze out starts. Thus the
two different regimes in the MTL model are qualitatively validated from the experimental evidence and MD simulations. The first regime is a hydrodynamic contact regime with the mobile lubricant layer, which behaves as a semi-solid at high shear rates, and the second regime is the squeeze-out or rupture of the bonded lubricant molecules, resulting in the initiation of solid contact.

In the presence of MTL layers, the sub-boundary lubrication (SBL) model [18] is used to account for the adhesive forces. As the disk surface in a HDD is atomically smooth, the lubricant thickness reaches a critical point (when adhesion increases rapidly) at very small lubricant thickness [19]. Adhesive interactions are modeled by a Lennard-Jones surface potential [20], since a large amount of energy is associated with the formation of a unit area of solid-lubricant interface, and the energy cost of liquid bridge formation is too high and meniscus formation is energetically unfavorable [19]. The adhesive force and pull-off force are highest for the smoother interface and separations below 2 nm [11]. Experimental work also showed that the surface energy of MTL layers on solid substrates is not constant but varies with penetration into the lubricant layer [10]. The MTL model has been extended to account for surface roughness [21], which is modeled using an extension of the statistical Greenwood-Williamson (GW) formulation (which also accounts for elastic-plastic contact).

The MTL model however does not account for the heating of the lubricant which can be caused by flash temperature and viscous friction. Archard et al. [22] have shown that the temperature difference within the film is the largest transient temperature in the contact region and it may be more than five times greater than the solid surface flash temperature. The heat generated by one pair of contacting asperities has been shown to be extremely small; contrary to the flash temperature, viscous heating effects have proved to be extremely important [23]. Spikes
et al. [24] observed that the heat generated from compression is very small in comparison to the heat caused by shearing under sliding conditions. Compared with iso-viscous models, significant reductions of film thickness and friction forces, especially in regions of high surface speeds, were observed beyond the predictions of conventional pressure-viscosity relationships. At high speeds, the rise in maximum temperature is more than 90% for a mixed lubricated system and depends on the surface roughness and sliding speed [25]. Through the analysis of thermal effects on Z-DOL lubricant using TOF-SIMS analysis, it was found that when Z-DOL lubricant is heated during operation its temperature is higher than the operating temperature [26]. Thus from various experiments and modeling investigations, evidence is present regarding the MTL heating during operation.

Using the MTL formulation to account for maximum stiffness and bearing forces that the lubricant can sustain, in this work, we present a study using design-of-experiments/analysis-of-variance (DOE/ANOVA) methodologies [27]. The study is three-dimensional: three parameters (that affect lubricant stiffness), sliding velocity, MTL viscosity and radius of gyration, are varied between three levels (-1, 0 and +1). The parametric study yields predictive models that can be used to determine the optimum combinations of these parameters that would give the maximum possible MTL lubricant bearing performance.

1.2 Nano-tribological behavior of hafnium-diboride thin films

Advanced hard protective coatings are required in the field of air-conditioning and refrigeration compressors, microelectromechanical systems (MEMS), magnetic storage devices, drawing dies and punches used in metal cutting and forming. These coatings can be used at unlubricated /dry conditions and can still possess low coefficient of friction, low wear rates and
high corrosion resistance [28-31]. For these applications, HfB$_2$, HfBN and HfBN/HfB$_2$-multilayer thin coatings were deposited using CVD technique. A single source precursor, Hf(BH$_4$)$_4$ is used to deposit HfB$_2$. The addition of nitrogen atoms produced by a remote plasma source to the CVD process creates ternary Hf-B-N films with N contents. The deposition temperature is 400°C and the samples were annealed at 700°C. From the investigation we have seen that annealing has improved mechanical and tribological properties.

It is important to understand the substrate effect in measuring mechanical properties of the coatings [32]. Previously wear resistance, high critical loads for delamination and low cohesive force as well as high hardness was reported for physical vapor deposition (PVD) grown Titanium-Boride and Titanium-Boron-Nitrides [33-37]. Hech et al. [6] found TiB, to be most qualified to transform and machine aluminium, TiAlB(N) promises to be a suitable coating to transform brass. The results show that TiAl(N)-coatings seems to be qualified for the transforming of steel. Rebholz et al. [35] could not find any correlation between BN content and coefficient of friction (COF). Nanoindentation and nanoscratch experimental techniques have been employed to measure hardness, reduced modulus and COF [38]. Wear depth after scratch is also measured for investigating elastic recovery of the scratches.

In the present work, single and multilayered HfB$_2$ coatings as deposited and following annealing (at 700°C) were studied in terms of their nano-mechanical properties. Characterization tools, such as scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used to gain insight about the thickness and the chemical environment of the coatings, respectively. The HfBN films are ~100 nm thick whereas the multilayer HfBN/HfB$_2$ are ~680 nm.
CHAPTER 2

Rough Surface with MTL Modeling

2.1 Rough surface modeling

The ISBL model [9, 10] does not account for the load bearing capacity of the lubricant, which was accounted for in the MTL model. During operation, the head and disk can remain separated or can be in contact as shown in the overall HDD schematic in figure 2.1 and the HDI schematic in figure 2.2. The semi-solid lubricant has two regimes of contact and follows the rough topography of the substrate, with 99.7% of which is circumscribed within $3\sigma$ from the mean of surface heights [9]. The thickness of the MTL layer is $t$, of which the bonded thickness of the lubricant is considered to be equal to twice the radius of gyration, $\kappa$ of the lubricant. Thus, the total thickness of the bonded lubricant is $2\kappa$ and the thickness of the mobile lubricant layer is $t-2\kappa$ as shown in the schematic of figure 2.3. The roughness of the surface is accounted for using a statistical model: An equivalent rough surface composed of a statistically large number of spherical asperities of the same radius $R$ and varying height according to a normal distribution, making contact with a rigid flat surface [39]. The single asperity model, which is used as a ‘cell’ in the statistically rough surface model, is shown in figure 2.4.

Fig. 2.1: Hard-disk drive schematic
Fig 2.2: Schematic of the HDI showing the relevant forces under (a) flying without contact and (b) contact conditions.

Fig 2.3: Schematic of rough lubricated surface topography

Fig 2.4: Schematic of a rigid smooth sphere moving in a viscous fluid of thickness, $t$ parallel to a plane
In displacement control dynamic shearing experiments we observe three regimes of contact: (a) Steady lubricant contact, (b) steady solid contact and (c) transition between the two regimes. Here ‘h’ is the separation between the mean of the surface heights of the two solids. We obtain the three regimes of contact by $3\sigma + 2\kappa \leq h < 3\sigma + t$, $3\sigma \leq h < 3\sigma + 2\kappa$ and $h > 3\sigma$ as shown in the schematic of figure 2.5. Here $h = h_o + 3\sigma$, where $h_o$ is the solid-solid gap (figure 2.3). Under certain conditions, lubricant forces are maximized when the solid-solid gap becomes equal to $2\kappa$; after that the lubricant is considered to breakdown and become expelled from the substrate, providing almost no resistance [16], until solid contact is initialized. Research has shown that under very high shear rates and solid confinement, MTLs exhibit solid-like behavior [7]. Therefore MTL films under high shear rate would be expected to have measurable normal and shearing stiffnesses.

Fig 2.5: Regimes of contact [the blue line indicates stiffness of the lubricant in the different regimes]
The MTL model formulation is given in Section 2.3. The disk and slider material and roughness properties are listed in table 2.1 and the dynamic parameters are given in table 2.2. These values were obtained from roughness, nanoindentation, and dynamic measurements [6].

Table 2.1: Disk and slider material and roughness properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{Disk}}$</td>
<td>Disk (DLC) Young’s modulus</td>
<td>280</td>
<td>GPa</td>
</tr>
<tr>
<td>$\nu_{\text{Disk}}$</td>
<td>Disk (DLC) Poisson ratio</td>
<td>0.240</td>
<td>-</td>
</tr>
<tr>
<td>$E_{\text{TFC}}$</td>
<td>TFC Young’s modulus</td>
<td>280</td>
<td>GPa</td>
</tr>
<tr>
<td>$\nu_{\text{TFC}}$</td>
<td>TFC Poisson ratio</td>
<td>0.240</td>
<td>-</td>
</tr>
<tr>
<td>$H$</td>
<td>Disk (DLC) hardness</td>
<td>13</td>
<td>GPa</td>
</tr>
<tr>
<td>$\Delta\gamma$</td>
<td>Surface adhesion energy</td>
<td>0.055</td>
<td>N/m</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Combined RMS roughness</td>
<td>0.36</td>
<td>nm</td>
</tr>
<tr>
<td>$R$</td>
<td>Combined mean radius of asperity curvature</td>
<td>0.276</td>
<td>μm</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Combined areal density of asperities</td>
<td>0.270</td>
<td>μm^2</td>
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<tr>
<td>$R_o$</td>
<td>Probe radius</td>
<td>102</td>
<td>μm</td>
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Table 2.2: Dynamic parameters of the slider and disk

<table>
<thead>
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<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
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<tr>
<td>$U_o$</td>
<td>Experimental shearing velocity</td>
<td>200</td>
<td>$\mu$m/s</td>
</tr>
<tr>
<td>$\kappa_o$</td>
<td>Minimum liquid gap (disp. Ctrl)</td>
<td>102</td>
<td>Mm</td>
</tr>
<tr>
<td>$\dot{\gamma} = U_o / \kappa_o$</td>
<td>Limiting shear rate</td>
<td>$2 \times 10^5$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$M$</td>
<td>Fitting coefficient</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>Fitting coefficient</td>
<td>$1.46 \times 10^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>$U$</td>
<td>Sliding velocity at the HDI</td>
<td>21.8</td>
<td>m/s</td>
</tr>
</tbody>
</table>

2.2 Temperature Effect on Viscosity

The confined MTL under high shear rates behaves differently than the bulk [40]. Based on modeling work, we have found that the MTL viscosity is 5×-8× of the bulk viscosity at the operating temperature. Also, the bulk viscosity of the PFPE lubricant used in this study (Z-tetraol with a molecular weight of about 2,700) was measured at different temperatures. A cubic polynomial is fitted in natural log of bulk viscosity vs. natural log of temperature, as shown in figure 2.6. From this model, we can find the bulk viscosity of the lubricant at higher temperatures as desired. At different temperatures the lower and higher limit of MTL viscosity is calculated (considering 5×-8× of bulk viscosity) and maximum forces and stiffnesses at these limits are shown in table 2.3.
Fig. 2.6: Experimentally measured bulk viscosity of PFPE at different temperatures; (a) measured data in linear plot; (b) the same data in logarithmic scales and fitted polynomial

Table 2.3: Maximum forces and stiffnesses at different temperature values

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Maximum normal bearing force, $P$ (mN)</th>
<th>Maximum shear force, $Q$ (µN)</th>
<th>Maximum bearing stiffness, $K_P$ (N/µm)</th>
<th>Maximum shear stiffness, $K_Q$ (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 °C</td>
<td>82.81±19.11</td>
<td>16.34±3.36</td>
<td>56.72±13.09</td>
<td>87.1±0</td>
</tr>
<tr>
<td>60 °C</td>
<td>28.45±6.57</td>
<td>6.76±1.15</td>
<td>19.49±4.49</td>
<td>87.1±0</td>
</tr>
<tr>
<td>80 °C</td>
<td>11.08±2.56</td>
<td>3.70±0.45</td>
<td>7.59±1.75</td>
<td>87.1±0</td>
</tr>
<tr>
<td>100 °C</td>
<td>4.58±1.17</td>
<td>2.57±0.19</td>
<td>3.20±0.74</td>
<td>87.1±0</td>
</tr>
<tr>
<td>120 °C</td>
<td>2.30±0.53</td>
<td>2.15±0.09</td>
<td>1.57±0.36</td>
<td>87.1±0</td>
</tr>
<tr>
<td>150 °C</td>
<td>0.84±0.19</td>
<td>1.89±0.04</td>
<td>0.58±0.13</td>
<td>87.1±0</td>
</tr>
</tbody>
</table>
2.3 The MTL model

According to the MTL model, the expressions for normal ($P$) and shearing ($Q$) forces are given by equation 2.1 and 2.2 respectively. Where $P_o$ and $Q_o$ are the maximum experimental normal and shear forces given by equations 2.3 and 2.4. The experimental shearing velocity $U = 200 \, \mu\text{m/s}$; the radius of spherical shearing probe $R = 102 \, \mu\text{m}$ [7]. Then the critical shear rate is $U/\kappa = 2 \times 10^5 \, /\text{s}$ for $\kappa = 1 \, \text{nm}$ [1].

\[ P_{tube} = P_o \left( \frac{\dot{\gamma}}{\dot{\gamma}_o} \right)^m \]  

(2.1)

\[ Q_{tube} = n \log \left( \frac{\dot{\gamma}}{\dot{\gamma}_o} \right) + Q_o \]  

(2.2)

\[ P_o = \frac{6\pi}{5} \mu_o U \sqrt{\frac{2R^3}{\kappa}} \]  

(2.3)

\[ Q_o = \frac{16\pi}{5} \mu_o UR \log \left( \frac{\kappa}{R} \right) \]  

(2.4)

The fitting coefficients $m$ and $n$ are calculated from equations 2.5 and 2.6 and can also be obtained from the logarithmic curves of normal and shear forces vs. shear rate.

\[ m = \frac{\log \left( \frac{P_{tube,2}}{P_{tube,1}} \right)}{\log \left( \frac{\dot{\gamma}_2}{\dot{\gamma}_1} \right)} \]  

(2.5)

\[ n = \frac{Q_{tube,2} - Q_{tube,1}}{\log \left( \frac{\dot{\gamma}_2}{\dot{\gamma}_1} \right)} \]  

(2.6)
The normal and shear stiffnesses are calculated according to equations 2.7 and 2.8. Where the shear rate is found from expression 2.9, \( U/d_o \) becomes maximum when the solid-solid gap reaches the bonded lubricant thickness \((2\kappa)\).

\[
k_p = \left| \frac{\partial P_{tube}}{\partial d_o} \right| = \frac{mP_o}{U\dot{\gamma}^m} \tag{2.7}
\]

\[
k_Q = \left| \frac{\partial Q_{tube}}{\partial d_o} \right| = \frac{n}{U \ln(10)} \dot{\gamma} \tag{2.8}
\]

\[
\dot{\gamma} = \frac{U}{d_o} = \frac{U}{h - 3\sigma - \kappa} \tag{2.9}
\]

Here \(d_o\) is the liquid gap. The maximum shear rate is when \(d_o = \kappa\), i.e., \(h - 3\sigma = 2\kappa\) (when the distance between slider and disk becomes twice the bonded lubricant thickness).

As viscosity changes logarithmically with temperature, the range of MTL viscosity values (5×-8× of bulk viscosity) is significantly larger for lower temperatures. With increasing temperature, this range decreases exponentially. Though the operating temperature of the HDD is 5 to 50 °C [41], at the asperity/contact level it can be as high as 250 °C [20] due to flash temperatures. Also, a temperature hike of two to three times the operating temperature is observed, as a consequence of frictional heating [23]. Accounting for the effects of frictional heating and flash temperature, we assume that local temperatures at the contact range between 90 and 120°C. Consequently, the range of MTL viscosity is found to be 0.4 ± 0.2 Pa-s and the normal bearing force, calculated through the MTL model (using equation 2.1), is 5.4 ± 2.6 mN. It is also apparent that both the temperature and the MTL/bulk viscosity ratio are very important in the calculation of the maximum bearing force. The shear force is calculated using equation 2.2
and the values are $2.7 \pm 0.5 \, \mu N$. The shear force is negligible in comparison to the normal bearing force. For the MTL viscosity range of $0.4 \pm 0.2 \, \text{Pa-s}$, the normal bearing stiffness is found to be $3.65 \pm 1.85 \, \text{N/µm}$.

An important phenomenon with the new lubricant property is that even at a temperature of 40 °C, the MTL stiffness value is reasonable, with a normal stiffness value corresponding to 0.82 nm of penetration into the solid substrate (stiffness = $50 \times 10^6 \, \text{N/m}$ [7]). As shearing stiffness is not a function of viscosity (i.e., temperature and MTL viscosity ratio), its value is constant for a uniform radius of gyration of the lubricant. However the higher the radius of gyration is, the lower is the shearing stiffness (for, $\kappa=0.73$, 0.94 nm; $K_q=87.1$, 67.64 N/m respectively). The lubricant properties are given in table 2.4.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>Thickness of the MTL</td>
<td>1.1</td>
<td>nm</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Radius of gyration</td>
<td>0.73 and 0.94</td>
<td>nm</td>
</tr>
<tr>
<td>$BR$</td>
<td>Bonding ratio</td>
<td>0.5 and 0.85</td>
<td>-</td>
</tr>
<tr>
<td>$C$</td>
<td>Coverage</td>
<td>80-85%</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_o$</td>
<td>Limiting viscosity</td>
<td>0.2-0.6</td>
<td>Pa-s</td>
</tr>
</tbody>
</table>

2.4 Parametric Study

DOE/ANOVA methodologies were used to generate accurate prediction models for the HDI system behavior using the improved MTL model and the obtained viscosity properties. A $3^3$
full factorial design was implemented where three lubricant and operating parameters, \( \mu, \kappa, U \), were varied at three levels, -1, 0, and +1. Using this methodology, any desired simulation output (response variable) could be analyzed (i.e., bearing and shear forces and normal and shear stiffnesses). The three levels of MTL viscosity (\( \mu \)), radius of gyration (\( \kappa \)) and sliding velocity (\( U \)) corresponding to -1, 0 and +1 level values are given in table 2.5.

<table>
<thead>
<tr>
<th></th>
<th>Level -1</th>
<th>Level 0</th>
<th>Level +1</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTL viscosity, ( \mu ) (Pa-s)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>MTL radius of gyration, ( \kappa ) (nm)</td>
<td>0.365</td>
<td>0.73</td>
<td>1.095</td>
</tr>
<tr>
<td>Sliding velocity, ( U ) (m/s)</td>
<td>10.5</td>
<td>21.0</td>
<td>31.5</td>
</tr>
</tbody>
</table>

To check the validity of the predictive models, residual analyses were performed whereby the residual errors were checked for the presence of non-random patterns. It is necessary for one of the three parameters \( \mu, \kappa, U \) to be held constant at each distinct level (-1, 0 and +1) to formulate a predictive model. However, the choice of constant parameter plays a major role in the accuracy of the predictive model. For example, we choose to keep \( \mu \) constant at each level by examination of the corresponding residual plots, resulting in three predictive equations that are functions of \( \kappa \) and \( U \). Hence, the parameter to be kept constant in each case was chosen by careful analysis of the residual plots so as to remove any bias.

The predictive fifth order model equation for \( y \) has the general form (2.10):

\[
y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 + b_{111} x_1^3 + b_{112} x_1^2 x_2 + b_{122} x_1 x_2^2 + b_{222} x_2^3 + \ldots + b_{22222} x_2^5
\]

(2.10)
To calculate the predicted value of $y$ for forces or stiffnesses (here, $y = P, Q, K_P, K_Q$) first the coefficient vector $b = (x \cdot \hat{x})^T \cdot \hat{y}$ is calculated, where $x$ and $y$ are the input factor and output response vectors respectively and denotes the dot product [27]. Here, in table 2.6, $b$ are the model coefficients for predicting maximum bearing force, $P_{\text{max}}$ for three levels of $\kappa$ and $x_1, x_2$ are the coded values of the varied parameters (here $x_1 = \mu$, $x_2 = U$). In the same way maximum bearing force for three levels of $\mu$ and $U$ can be calculated using the coefficients given in table 2.6-2.8. A fifth order model was proved sufficient to capture the main and confounded effects.

Table 2.6: Predictive model results and residual errors for three different levels of $\kappa$

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_{11}$</th>
<th>$b_{12}$</th>
<th>$b_{22}$</th>
<th>$b_{111}$</th>
<th>$b_{112}$</th>
<th>$b_{222}$</th>
<th>$b_{1111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.2432</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1701</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.0004</td>
<td>0</td>
<td>0.1526</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_{1112}$</th>
<th>$b_{1122}$</th>
<th>$b_{2222}$</th>
<th>$b_{11111}$</th>
<th>$b_{11122}$</th>
<th>$b_{11222}$</th>
<th>$b_{12222}$</th>
<th>$b_{22222}$</th>
<th>Residual error</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>-0.0144</td>
<td>0</td>
<td>-0.0319</td>
<td>0</td>
<td>0</td>
<td>0.0002</td>
<td>-0.0002</td>
<td>0.0044</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-0.0100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0002</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>-0.0091</td>
<td>0</td>
<td>-0.2867</td>
<td>0</td>
<td>0</td>
<td>0.0002</td>
<td>-0.0005</td>
<td>0.0219</td>
</tr>
</tbody>
</table>

The coefficients for predicting the maximum bearing force for the three levels of $U$ are given in table 2.7.
The coefficients for predicting the maximum bearing force for the three levels of $\mu$ is given in table 2.8.

Table 2.7: Predictive model results and residual errors for three different levels of $U$

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_{11}$</th>
<th>$b_{12}$</th>
<th>$b_{22}$</th>
<th>$b_{111}$</th>
<th>$b_{112}$</th>
<th>$b_{122}$</th>
<th>$b_{222}$</th>
<th>$b_{1111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-0.0206×10$^7$</td>
<td>0</td>
<td>0</td>
<td>-0.7135×10$^7$</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.096×10$^7$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>0.0205×10$^7$</td>
<td>0</td>
<td>0</td>
<td>-1.41×10$^7$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_{1112}$</th>
<th>$b_{1122}$</th>
<th>$b_{1222}$</th>
<th>$b_{11111}$</th>
<th>$b_{11112}$</th>
<th>$b_{11222}$</th>
<th>$b_{12222}$</th>
<th>$b_{22222}$</th>
<th>$b_{22222}$</th>
<th>$b_{11111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>-0.1427×10$^7$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1926×10$^{-3}$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.267×10$^{-3}$</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>0.1427×10$^7$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.326×10$^{-3}$</td>
</tr>
</tbody>
</table>

The coefficients for predicting the maximum bearing force for the three levels of $\mu$ is given in table 2.8.

Table 2.8: Predictive model results and residual errors for three different levels of $\mu$

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_{11}$</th>
<th>$b_{12}$</th>
<th>$b_{22}$</th>
<th>$b_{111}$</th>
<th>$b_{112}$</th>
<th>$b_{122}$</th>
<th>$b_{222}$</th>
<th>$b_{1111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>$b_{1112}$</th>
<th>$b_{1122}$</th>
<th>$b_{1222}$</th>
<th>$b_{11111}$</th>
<th>$b_{11112}$</th>
<th>$b_{11222}$</th>
<th>$b_{12222}$</th>
<th>$b_{22222}$</th>
<th>$b_{22222}$</th>
<th>$b_{11111}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>-0.57×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.015×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-1.12×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
<td>-1.7×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.045×10$^3$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
CHAPTER 3

Results and discussion of DOE/ANOVA of MTL model

3.1 Introduction

For the three varying parameters $\mu$, $\kappa$, $U$, the effects of variation from level -1 to +1 is shown in table 3.1. The comparison is done with the zero level values of $P$, $Q$, $K_P$, $K_Q$ by taking the ratio (in percentage) of total change and zero level value for each of the four parameters. At high shear rates the lubricant behaves like a semi-solid and can withstand bearing and shear forces [6]. Viscosity affects mostly the force sustainability capacity of the lubricant, whereas radius of gyration affects the normal and shearing stiffnesses. With the increase of viscosity the lubricant provides more constrain to penetration. The smaller the $\kappa$, the larger the mobile lubricant layer thickness and this mobile lubricant is responsible for increasing the lubricant stiffness. All forces and stiffnesses decrease with the increase of radius of gyration. Thus it is important to select a lubricant with lower $\kappa$: between the two PFPE lubricants available with $\kappa$ values of 0.73 and 0.94 nm, the lubricant with $\kappa = 0.73$ nm would be the better choice. With the increase of sliding velocity, the bearing and shear forces, as well as the normal stiffness, increase. The sliding velocity, due to the MTL model formulation, has no effect on the shear stiffness. Physically, this could be attributable to the interfacial slip velocity having reached its maximum value beyond the critical shear rate [31]. Among the three parameters, the bearing and shear forces are most sensitive and increase with increasing viscosity. As discussed earlier, we want the bearing force to be high so that the lubricant can potentially provide sufficient wear protection to the interface; hence, it is very important to maintain high viscosity.
Table 3.1: Comparison of forces and stiffnesses between -1 to +1 levels

<table>
<thead>
<tr>
<th>Difference between maximum and minimum value</th>
<th>For change of radius of gyration, $\kappa$</th>
<th>For change of sliding velocity, $U$</th>
<th>For change of limiting viscosity, $\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal force, $P$ (mN)</td>
<td>3.2</td>
<td>2.8</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>(60%)</td>
<td>(52%)</td>
<td>(101%)</td>
</tr>
<tr>
<td>Shear force, $Q$ (μ N)</td>
<td>0.16</td>
<td>0.16</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>(6%)</td>
<td>(6%)</td>
<td>(35%)</td>
</tr>
<tr>
<td>Normal stiffness, $K_P$ (MN/m)</td>
<td>8.4</td>
<td>1.9</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>(228%)</td>
<td>(52%)</td>
<td>(101%)</td>
</tr>
<tr>
<td>Shear stiffness, $K_Q$ (N/m)</td>
<td>116.13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(133%)</td>
<td>(0%)</td>
<td>(0%)</td>
</tr>
</tbody>
</table>

3.2 Design of Experiments/Analysis of Variance (DOE/ANOVA) Results

The maximum bearing forces at the three different levels of $\mu$, $\kappa$, $U$ are shown in figures 7, 8 and 9. The DOE results can be subdivided into three cases.

- Case 1: Variation of $\mu$ and $U$ for three levels of $\kappa$
- Case 2: Variation of $\kappa$ and $\mu$ for three levels of $U$
- Case 3: Variation of $\kappa$ and $U$ for three levels of $\mu$
3.2.1 Case 1 (DOE analysis for fixed $\kappa$)

In this case $\mu$ and $U$ are varied for three levels of $\kappa$ as shown in figure 3.1. The maximum bearing force increases sharply with the increasing limiting viscosity, but with the increase of shearing velocity the increment is negligible compared to the change caused by viscosity. Thus, a change of viscosity plays dominant role. High viscosity of the lubricant is possible by choosing a highly viscous lubricant. However if that compromises other benefits of PFPE (increasing viscous shear), then the high temperature induced in the slider disk contact needs to be cooled down. Another design recommendation is to use a lubricant that will be more resistant to heating.

3.2.2 Case 2 (DOE analysis for fixed $U$)

$\kappa$ and $\mu$ are varied for three levels of $U$, as shown in figure 3.2. The maximum bearing forces decrease with the increment of radius of gyration and increase with increasing limiting viscosity. Also, in this case the effect of $\mu$ is more prominent than that of $\kappa$. This analysis is done considering that the total thickness of the lubricant is the same and only the bonded lubricant thickness ($=2\times$radius of gyration) is varied. Nevertheless the lubricant with lower bonded thickness exhibits better bearing capability.

3.2.3 Case 3 (DOE analysis for fixed $\mu$)

In figure 3.3 the variation of $\kappa$ and $U$ for three levels of $\mu$ is shown. The maximum bearing forces decrease with the increase of the radius of gyration. The bearing forces increases with the increase of shearing velocity, however in between it shows complex behavior. In consequence to this the maximum sliding velocity that can be attainable without hindering the read/write performance should be employed.
Fig 3.1: Parametric plots of the maximum bearing forces for three different levels of radius of gyration $\kappa$ (Case 1)
Fig 3.2: Parametric plots of the maximum bearing forces for three different levels of shearing velocity $U$ (Case 2)

Fig 3.3: Parametric plots of the maximum bearing forces for three different levels of limiting viscosity $\mu$ (Case 3)
3.3 Residual analysis

From the residual analysis (given in section 2.4), case 1, which is the parametric study with different levels of radius of gyration, gives minimum error, while residuals are randomly oriented for changes of individual parameters. However, if the varying parameter needed for design is $\mu$ or $U$ then case 2 or 3 of the study can be used respectively.
CHAPTER 4

Experimental Procedure for the Hafnium Boride thin films

4.1 Film deposition and growth

Thin films of HfB$_2$ were deposited by thermal CVD of Hf(BH$_4$)$_4$ in an ultra-high vacuum (UHV) chamber [43]. The addition of nitrogen (8-20%) atoms is incorporated using remote plasma source. The multilayer of HfBN/HfB$_2$ on silicon was created by cycling the remote plasma off and on during growth [44]. When deposited at temperatures < 400°C, the as-deposited films are amorphous in X-ray diffraction measurements. The films crystallize upon annealing to 700°C, however the resulting grain diameter is only ~5nm, as revealed by lattice imaging high resolution TEM (HRTEM). The lack of grain coarsening probably reflects the low homologous temperature; since bulk Hafnium-Borides melts at ≥ 3500 K, annealing at 700°C corresponds to a low value of $T/T_{\text{melt}} = 0.28$. These films are essentially stoichiometric and impurity-free, smooth on the nm scale and highly conductive. By adjusting the growth parameters, good conformal coverage, on features with aspect ratio ≤ 5:1, can be obtained at growth rates up to 200 nm/min. Cross section SEM and TEM images are given in figure 4.1, showing the morphology and thickness of the films.
Fig. 4.1: SEM and TEM cross section images of the samples

4.2 Nanoindentation and nanoscratch

Berkovich nanoindentation measurements, restricted to a depth that is <20% of the film thickness and calibrated against Fused-Quartz (FQ), were carried out on the obtained samples. The nanoindentation was performed using a TI-950TriboIndenter® equipped with a standard transducer. This transducer has a maximum load limit of ~12 mN and maximum displacement of ~4.5 μm. The Berkovich tip is a three sided pyramid with semi-vertical angle of 70°. The most important criterion for indentation measurement is the calibration of the tip, known as area function. The Oliver –Pharr [45] compliance method is utilized for measuring the area function. The contact depth ($h_c$) is the only information given by indentation measurement. The tip area function correlates the contact area to the contact depth. This relationship needs to be determined
for the Berkovich tip during measurement. For a perfect tip shape, the area function would be the geometrical function as in equation (1) [46].

\[ A_c(h_c) = 24.5h_c^2 \] (4.1)

However due to tip imperfections, for the Berkovich tip the area function usually takes the form of equation (2).

\[ A_c(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/4} + C_3 h_c^{1/8} + C_4 h_c^{1/16} + C_5 h_c^{1/32} \] (4.2)

The polynomial curve-fitting during the experimental procedure is given in figure 4.2.

![Fig. 4.2: Area function for Berkovich tip](image)

The nanoscratch technique was utilized to measure the coefficient of friction and wear depth (in µm). To eliminate the effect of tip geometry, a conospherical (870 nm tip radius) tip was used for nanoscratch. The scratches were done under constant normal loads of 100, 200, 350 and 500 µN at the rate of 0.33 µm/s. The wear length was 10 µm. After the scratch experiments
were done the wear scars were rescanned (at a much lower load) using the same tip to estimate the post wear depth. This also gives an estimation of the elastic recovery of the wear.

4.3 Shear strength measurement from nano-scratch

The nanoscratch method is a useful tool for measuring adhesion. A sharp diamond tip is used to initiate the delamination of the coating with the combination of tip movement moving in vertical and horizontal directions along the surface. Various models have been developed to determine the shear strength as well as the energy release rate at the interface from a scratch test. The applicability of these models depends on the failure mode observed. Benjamin and Weaver [47, 48] analyzed the interfacial shear strength produced at the coating-substrate interface for coating removal given by

\[
\tau_c = \left( \frac{HP_c}{\pi r^2 - (Pc/\pi H)} \right)^{1/2}
\]  

(4.3)

Where \( \tau_c \) is the shearing force per unit area to delaminate the coating given in terms of the substrate hardness \( H \), the critical applied load \( P_c \) and the radius of the stylus \( r \). This analysis is applicable when substrate deforms plastically.

4.4 Morphology of the films (SEM)

The morphology and thickness of the films were characterized by scanning electron microscopy (SEM). SEM images were obtained using a JEOL 6060 at an operational voltage of 10 keV. The samples were cleaned and sputtered coated before imaging.
4.5. Roughness of the films (AFM)

A Digital Instruments Dimension 3100 Atomic Force Microscope (AFM) was utilized to measure the surface roughness. The root-mean-square (rms) roughness was determined from ten measurements obtained from different areas of each film.

4.6 Surface analysis (XPS)

XPS analysis was conducted on a Perkin Elmer PHI 5400 spectrometer equipped with a hemispherical electron analyzer and a non-monochromatic Mg Kα X-ray source (1253.6 eV). All reported photoelectron binding energies are referenced to the C 1 s feature of adventitious carbon at 285 eV (internal standard) to take into account charging effects. XPS studies were performed inside and outside the wear tracks of the gray cast iron surfaces and on the gray cast iron pins (counter surface). The survey spectra were acquired at pass energy of 178.95 eV. A certain region of the spectrum was scanned a number of times to obtain a good signal-to-noise ratio (the detailed scan was performed at a pass energy of 35.75 eV). The measurements were performed in three different areas inside the wear track for each individual sample for repeatability purposes. The peak fitting was performed using Casa XPS (version 2.3.14) software.
5.1 RMS roughness

The RMS roughness is measured using contact mode AFM (table 5.1). The roughness value of the HfB$_2$ is the lowest among the three samples. The AFM image is shown in figure 5.1. HfB$_2$ has an RMS (2.18-2.56 nm) roughness compared to HfBN and HfBN/HfB$_2$ (4.7-7.63 nm) samples. Annealed samples for HfB$_2$ and HfBN/HfB$_2$ have lower RMS roughness in comparison to the as-deposited once. This is probably due to crystallization due to annealing.

<table>
<thead>
<tr>
<th></th>
<th>As-deposited</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfBN</td>
<td>5.38</td>
<td>7.63</td>
</tr>
<tr>
<td>HfBN/HfB$_2$</td>
<td>5.71</td>
<td>4.7</td>
</tr>
<tr>
<td>HfB$_2$</td>
<td>2.56</td>
<td>2.18</td>
</tr>
</tbody>
</table>
5.2 Hardness and Reduced Modulus

The TI 950 Hysitron tribonanoindenter with a standard transducer and Berkovich tip was used to measure hardness and reduced modulus. The area function (Figure 4.2) was determined using multiple indentations on fused quartz (FQ). 16 indentations starting from 100 µN to 1700 µN were employed on FQ. Multiple indentations with constant increasing load of 50 µN starting from 50 µN upto 500 µN was employed and the depth of penetration was below 20% of the total thickness to avoid substrate effects. From figure 5.2 and 5.3, HfB₂ possessed higher hardness (21.6 GPa) and modulus (219.5 GPa) in comparison to the HfBN (H = 14.6 GPa, Eᵣ = 173.8 GPa) and HfBN/HfB₂ (H = 12.9 GPa, Eᵣ = 147.68 GPa) films. The above values are for annealed
samples. Between the as-deposited and annealed films the annealed once have higher hardness and modulus. Thus crystallization using annealing has improved the mechanical property.

Fig. 5.2: Reduced modulus
5.3 Nanoscratch

5.3.1 Load-dependence of friction and wear recovery

The micro-friction behavior was studied at different constant loads (100, 200 and 350 µN) at constant sliding velocity of 0.3um/s. With the increase of load the coefficient of friction (COF) increases as shown in figure 5.4. The error bars here are for standard deviation. The scratches are shown in figure 5.5. The COF increases about 0.1 with increasing load from 100 to 350 µN for most of them. Annealed samples have lower COF than the as-deposited once. The HfBN possessed lowest COF among the three compositions investigated in the herein study. To determine the wear recovery the constant load function with retrace was chosen. The retrace length was 2 µm more than the wear depth. The wear rescans are shown in the figures 5.6-5.8.
Fig. 5.4: Coefficient of friction at different loads

Fig. 5.5: Scratch images at different loads
**Fig. 5.6:** Scratch with retrace for HfB$_2$ samples

**As deposited (200 μN)**

**Annealed (200 μN)**

**As deposited (350 μN)**

**Annealed (350 μN)**

**Fig. 5.7:** Scratch with retrace for HfBN samples

**Annealed (200 μN)**

**Annealed (350 μN)**
Figures 5.9 and 5.10 give a summary of the wear depths with percentage of recovery for 200 µN and 350 µN. The as-deposited films exhibit a wear recovery of 31-39% whereas the annealed films %recovery is highly dependent on the film. HfBN and HfBN/HfB₂ showed really good wear recovery (52-86%) whereas HfB₂ showed really poor wear recovery.
Fig. 5.9: In situ depth and residual depth and the difference elastic recovery [load 200μN]

Fig. 5.10: In situ depth and residual depth and the difference elastic recovery [load 350μN]
5.3.2 Shear strength

The shear strength is measured at the critical load. The critical load \( (P_c) \) is found from the scratch test, and the load at the start of failure is termed as \( P_c \). The measurement of \( P_c \) is shown in figures 5.11-5.16. The annealed samples have 2-3 GPa higher shear strength values compared to the as-deposited ones. Among the three compositions studied herein, annealed HfBN possessed the highest shear strength. In table 5.2 the comparison of shear strength is provided. The importance of high shear strength is that the film will not readily delaminate.

Table 5.2: Shear strength of different samples

<table>
<thead>
<tr>
<th></th>
<th>Critical load, ( P_c ) (mN)</th>
<th>Shear strength, ( \tau_c ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfBN-asdeposited</td>
<td>49</td>
<td>3.24</td>
</tr>
<tr>
<td>HfBN-annealed</td>
<td>121</td>
<td>5.96</td>
</tr>
<tr>
<td>HfBN/HfB(_2)-asdeposited</td>
<td>53</td>
<td>2.78</td>
</tr>
<tr>
<td>HfBN/HfB(_2)-annealed</td>
<td>91</td>
<td>4.80</td>
</tr>
<tr>
<td>HfB(_2)-asdeposited</td>
<td>48</td>
<td>2.66</td>
</tr>
<tr>
<td>HfB(_2)-annealed</td>
<td>74</td>
<td>5.41</td>
</tr>
</tbody>
</table>
Caption is on following page
Fig. 5.11: Measurement of $P_c$ for as-deposited HfB$_2$ samples
Fig. 5.12: Measurement of $P_c$ for annealed HfB$_2$ samples
Fig. 5.13: Measurement of $P_c$ for as-deposited HfB$_2$/HfBN samples
Caption is on following page
Fig. 5.14: Measurement of $P_c$ for annealed HfB$_2$/HfBN samples
Fig. 5.15: Measurement of $P_c$ for as-deposited HfBN samples
Caption is on following page
Fig. 5.16: Measurement of $P_c$ for annealed HfBN samples
6.1 Molecularly Thin Lubricant Films in Magnetic Storage

Confined MTL layers under high shear rates have viscosity values that are five to eight times of the bulk viscosity at the operating temperature. Based on published research, we used a temperature of the MTL of 90-120 °C, corresponding to an MTL viscosity range of 0.4±0.2 Pa-s. The bearing and shear forces and stiffnesses were calculated using the MTL model and the bearing stiffnesses are within the expected range, compared to solid surface forces. The force and stiffnesses ascertain reasonable values compared to the literature. A $3^3$ full-factorial design was implemented to observe MTL behavior at different levels of $\mu$, $\kappa$, and $U$. From residual analysis, the error was found to be lowest by keeping $\kappa$ fixed and varying $\mu$ and $U$. A number of response surface plots were obtained through DOE nonlinear regression modeling. It was found that the maximum bearing forces are most sensitive to the increase of limiting viscosity. In comparison, the increment is undetectable for the increase of shearing velocity; whereas, bearing force declines with higher radius of gyration.

In summary, it is very important to maintain high viscosity by lowering the temperature of the slider-disk contact using adequate cooling or by employing lubricants with more resistance to heating (i.e., high viscosity of the MTL at elevated temperatures). In this manner, we can increase the bearing forces of the MTL sustainability, which is desirable as it will enable robust “surf” recording without solid contact and the possibility of wear and catastrophic failures. Hence optimum operating circumstance can be delineated for the HDD to accomplish maximum bearing capacity using this analysis.
6.2 Hafnium Boride Thin Solid Films

In the case of Hafnium Boride thin films, the annealed samples showed higher hardness and modulus compared to the as-deposited once. Among the three samples HfB$_2$, HfB$_2$/HfBN and HfBN the HfBN possessed lowest COF. In case of wear recovery HfBN and HfB$_2$/HfBN showed really good wear recovery compared to the HfB$_2$. Also if we compare shear strength then HfBN also possess highest shear strength. Thus addition of Nitrogen is beneficial from tribological point of view. In future XRD will be done to investigate chemical morphology of the films.
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