NANOTRIBOLOGICAL INVESTIGATIONS OF MATERIALS, COATINGS
AND LUBRICANTS FOR NANOTECHNOLOGY APPLICATIONS
AT HIGH SLIDING VELOCITIES

DISSERTATION

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* * * * *

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If

If you can keep your head when all about you  
Are losing theirs and blaming it on you;  
If you can trust yourself when all men doubt you,  
But make allowance for their doubting too;  
If you can wait and not be tired by waiting,  
Or, being lied about, don't deal in lies,  
Or, being hated, don't give way to hating,  
And yet don't look too good, nor talk too wise;  

If you can dream - and not make dreams your master;  
If you can think - and not make thoughts your aim;  
If you can meet with triumph and disaster  
And treat those two imposters just the same;  
If you can bear to hear the truth you've spoken  
Twisted by knaves to make a trap for fools,  
Or watch the things you gave your life to broken,  
And stoop and build 'em up with wornout tools;  

If you can make one heap of all your winnings  
And risk it on one turn of pitch-and-toss,  
And lose, and start again at your beginnings  
And never breath a word about your loss;  
If you can force your heart and nerve and sinew  
To serve your turn long after they are gone,  
And so hold on when there is nothing in you  
Except the Will which says to them: "Hold on";  

If you can talk with crowds and keep your virtue,  
Or walk with kings - nor lose the common touch;  
If neither foes nor loving friends can hurt you;  
If all men count with you, but none too much;  
If you can fill the unforgiving minute  
With sixty seconds' worth of distance run -  
Yours is the Earth and everything that's in it,  
And - which is more - you'll be a Man my son!

— Rudyard Kipling
The advent of micro/nanostructures and the subsequent miniaturization of moving components for various nanotechnology applications, such as micro/nanoelectromechanical systems (MEMS/NEMS), have ascribed paramount importance to the tribology and mechanics on the nanoscale. Most of these micro/nanodevices and components operate at very high sliding velocities (of the order of tens of mm/s to few m/s). Atomic force microscopy (AFM) studies to investigate potential materials, coatings and lubricants for these devices have been rendered inadequate due to the inherent limitations on the highest sliding velocities achievable with commercial AFMs (<250 μm/s). The development of a new AFM based technique, done as part of this research work, has allowed nanotribological investigations over a wide range of velocities (up to 10 mm/s). The impacts of this research on the design and development of nanotechnology applications are profound. Research conducted on various materials, coatings and lubricants reveals a strong velocity dependence of friction, adhesion and wear on the nanoscale. Based on the experimental evidence, theoretical formulations have been conducted for nanoscale friction behavior to design a comprehensive analytical model that explains the velocity dependence. The model takes into consideration the contributions of adhesion at the tip-sample interface, high impact...
velocity related deformations at the contacting asperities and atomic scale stick-slip. Dominant friction mechanisms are identified and the critical operating parameters corresponding to their transitions are defined.

Wear studies are conducted at high sliding velocities for materials, coatings and lubricants to understand the primary failure mechanisms. A novel AFM based nanowear mapping technique is developed to map wear on the nanoscale and the interdependence of normal load and sliding velocity on sample surface wear is studied. This technique helps identify and classify wear mechanisms and determine the critical parameters responsible for their transitions. The promising tribological properties exhibited by diamondlike carbon (DLC) coating and its role as a potential protective coating for nanotechnology applications are discussed. Scale dependence of micro/nano–friction and –adhesion is also studied. The primary reason for the scale dependence is the sample surface roughness and the higher contact pressures that are encountered on the nanoscale. This study emphasizes the fact that material behavior on one scale cannot be assumed to hold on another scale. The interdependence of mechanical and tribological properties for various materials has been explored and tribologically ideal materials with low adhesion and friction for nanotechnology applications have been identified.
Dedicated to my parents

Subhashchandra B. Tambe and Vijaya S. Tambe
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Nanotechnology, defined literally as any technology performed on a nanoscale that has applications in the real world (Feynman, 1960), has spurred the development of innovative micro/nanosystems with the discovery of novel materials, processes and phenomena on the micro/nanoscale and led to the rapid advancement of micro/nanoelectromechanical systems (MEMS/NEMS) and their various biological and biomedical applications, BioMEMS. Recent years have seen a multitude of new emerging applications in this field. Commercial applications such as the microfluidic devices that can manipulate tiny amounts of fluids, ‘lab-on-chip’ sensors used for drug delivery, accelerometers used for automobile air bag deployment and digital micromirror devices (DMDs) used in hi-definition TVs and video projectors in homes and theatres are just the tip of the iceberg. In fact these MEMS/NEMS are now believed to be the next logical step in the “silicon revolution”. Visionaries and leading scientists and researchers, presenting at the National Nanotechnology Initiatives (NNI) workshop on Nanotechnology in Space Exploration held in Palo Alto, CA (USA) in Aug 2004, have slated the emerging field of nanotechnology to be the next disruptive technology that will have major impact in the next one to three decades. It is estimated that the annual global
impact of products where nanotechnology will play a key role will exceed US$ 1 trillion by 2015 and would require about 2 million nanotechnology workers (Roco, 2003).

1.1 Micro/nanotribology

Despite the increasing popularity and technological advances in MEMS/NEMS applications the severe tribological (friction and wear) problems tend to undermine their performance and reliability. In fact, several studies have shown that the tribology and mechanics of these devices are the limiting factors to the imminent broad based impact of nanotechnology on our everyday lives (Komvopoulos, 2003; Maboudian and Howe, 1997; Bhushan, 1998, 2003, 2004). Miniaturization and the subsequent development of MEMS/NEMS require better tribological performance of the system components and a fundamental understanding of basic phenomena underlying friction, wear and lubrication on micro- and nanoscale (Bhushan, 1997, 1998, 1999a, b, 2001a, b, 2004). The components used in micro/nanostructures are very light (on the order of few micrograms) and operate under very light loads (on the order of few micrograms to a few milligrams). Going from macro to micro scale the surface area to volume ratio increases considerably and becomes a cause of serious concern from tribological point of view. On microscales surface forces such as friction, adhesion, meniscus forces, viscous drag and surface tension that are proportional to area, significantly increase and limit the life and reliability of MEMS/NEMS. As a result, friction and wear (on nanoscale) of lightly loaded micro/nanostructures are highly dependent on the surface interactions.

The emergence of the new field of micro/nanotribology, which pertains to the experimental and theoretical investigations of interfacial processes occurring during
adhesion, friction, wear and thin film lubrication of sliding surfaces on scales ranging from the atomic and molecular scale to the microscale, and its associated techniques (Bhushan, 1999a) has provided a viable means of addressing the tribological issues on micro/nanoscales. Micro/nanotribological investigations can be performed using the surface force apparatus (SFA) and the atomic force microscope (AFM) and have already provided valuable insights into the behavior of materials on the nanoscale (Bhushan et al., 1995; Bhushan, 1999a). A sharp tip of the AFM developed by Binnig et al. (1986), sliding on a surface simulates micro/nanoscale contacts, thus allowing high-resolution measurements of surface interactions.

1.2 Historical perspective for velocity dependence of friction

Controlling friction and wear is important in all machine components requiring relative motion. Two basic laws of dry (or conventional) friction are generally obeyed over a wide range of applications. These laws are often referred to as Amontons’ laws, after the French physicist Guillaume Amontons who rediscovered them in 1699 (Amonton, 1699); after Leonardo Da Vinci first described them some 200 years earlier. Amontons' first law states that the friction force is proportional to the normal load. The second law states that friction force (or coefficient of friction) is independent of the apparent area of contact between the contacting bodies. To these two laws, a third law is sometimes added which is often attributed to Coulomb (1785). It states that the kinetic friction force (or coefficient of friction) is independent of the sliding velocity once motion starts. Coulomb also made a clear distinction between static and kinetic friction. These laws have over the years been found to not hold in many cases (Bowden and
Various studies on the micro/nanoscale have indicated a strong normal load and sliding velocity dependence of friction force (Koinkar and Bhushan, 1996; Bhushan and Kulkarni, 1996; Bouhacina et al., 1997; Baumberger et al., 1999; Riedo et al., 2003; Liu and Bhushan, 2002, 2003; Gnecco et al., 2004; Tambe and Bhushan, 2004b, 2005a-i). As dimensions of the components and loads used, continue to decrease, tribological and mechanical properties on the micro- to nanoscale become very important. It is critical to evaluate MEMS/NEMS component materials and coatings for failures resulting from high static friction and adhesion (stiction). A fundamental understanding of nanoscale friction is of paramount importance, not only for the design of reliable industrial and scientific applications but also to provide a bridge between science and engineering on the micro/nanoscale.

1.2.1 Velocity dependence of friction from atomic to micro/nanoscales

Measurement of friction on the atomic scale with an AFM is often associated with the phenomenon of the atomic stick-slip, first observed by Mate et al. (1987) between a tungsten tip and graphite surface in ambient air. Friction studies on well-defined (i.e., atomically flat and ordered) samples have been carried out and atomic scale stick-slip behavior with lattice periodicity has been observed on a variety of samples of different nature and properties (Carpick and Salmeron, 1997). Tomanek et al. (1991) performed calculation of an atomically modulated friction force between a Pd tip and graphite surface with an AFM. It was shown that the friction force depended not only on the tip-sample interaction potential, but also even more critically on the construction parameters.
of the AFM such as cantilever spring constant. Johnson and Woodhouse (1998) reported a simple model explaining periodic variation of the atomic scale friction at the lattice spacing of the surface being studied. In the model for this behavior the “dynamic element” of the system is provided by the elastic stiffness and inertia of the cantilever, which supports the tip. The relation between the contact stiffness and the amplitude of the periodic friction force is derived in order for the stick-slip motion at the lattice periodicity to be achieved. Sliding friction between the tip of a friction force microscope and NaCl (100) was studied to deduce the velocity dependence of friction forces on the atomic scale (Gnecco et al. 2000, Bennewitz, et al., 2001). A logarithmic dependence of the mean friction force on velocity was revealed at low velocities. The experimental data were interpreted in terms of a modified Tomlinson model. It was also found that when a tip with high spring constant was used, no atomic features could be resolved. Friction on mica and HOPG was studied by means of AFM at sliding velocities up to 25 µm/s (Hoshi et al., 2000). A regular saw-toothed signal corresponding to atomic stick-slip was observed at sliding velocities less than 1.5 µm/s. At higher velocities, the stick-slip pattern disappeared. The dynamic behavior of the contact was dominated by the vibrational properties of the tip.

Zwörner et al. (1998) studied the velocity dependence of friction force with an AFM for different carbon compounds (diamond, graphite, amorphous carbon). The measured friction force was found to be constant over a range of sliding velocities from a few nm/s to a few tens of µm/s. Riedo et al. (2002) investigated the kinetics of capillary condensation in nanoscale sliding friction. A logarithmic dependence of friction force on the scan velocity was reported and it was found that while for partially hydrophilic and
nanoscale rough surfaces friction decreased logarithmically, for partially hydrophobic surfaces nanoscale friction increased with velocity. The studied velocity dependence was explained with the help of a model based on the kinetics of capillary condensation.

1.2.1.1 Velocity dependence studies with lubricants

Miniaturization of magnetic storage media, aimed at increasing data storage density and the rapid advancements in the development of intricate micro/nanostructures, puts natural limits on usage of ordinary bulk lubricants. They cannot effectively operate in conditions of confined geometry where many important parameters such as viscosity can deviate dramatically from the corresponding bulk values. Ultrathin organic films anchored to solid surfaces such as Langmuir-Blodgett (LB) films, self-assembled monolayers (SAM) and perfluoropolyethers (PTFE) lubricants are the objects of great interest as model lubricants and are potential candidates for lubrication of micro/nanostructures because of their compatibility with nanotechnology (Bhushan, 1999a, 2001a, b, 2004). Friction on atomic to micro/nanoscales has been measured for LB films, SAMs and PFPE lubricants at low and moderate sliding velocities (<250 µm/s) using AFM. Koinkar and Bhushan, (1996) found that the coefficient of friction for an unlubricated silicon sample and a sample lubricated with Z-15 lubricant decreased with an increase in the sliding velocity in ambient environment but remained insensitive to sliding velocities in dry environments. Samples lubricated with fully-bonded Z-DOL lubricant did not show any effect of sliding velocity on friction. Alignment of liquid molecules (shear thinning) was believed to be responsible for the drop in friction with an increase in sliding velocity for samples with mobile films in ambient environment.
Tsukruk et al. (1996) performed AFM evaluation of frictional characteristics of several types of boundary lubricants, which included LB monolayers of stearic acid and cadmium stearate, SAMs of alkylchlorosilanes, and molecularly thin films composed of a fullerene monolayer chemically attached to the functional surface of SAMs. SAMs were found to be much more stable but had the drawback of growth in the coefficient friction at high sliding velocities. Liu et al. (1996) observed variation of friction force with sliding velocity (which was varied from 0.01 to 20 µm/s) for SAMs formed from 11 double chain quaternary ammonium surfactants on mica. For some of the samples, coefficient of friction first increased with velocity and then reached a plateau. A different behavior was observed for the other samples, when the friction force displayed a peak at some critical velocity. This velocity dependent friction was correlated to chemical structure and chain melting temperature of the surfactant monolayers.

Brewer et al. (2001) performed AFM studies for a series of SAMs of alkanethiols of varying chain length and terminal groups absorbed on gold. It was found that the friction force between the chemically modified (SAM coated) tip and the sample surface increased with sliding velocity increasing before a plateau was reached. The initial rise in the friction force was more rapid for acid terminated SAMs as compared to methyl and hydroxyl terminated SAMs. The observations were explained in terms of stabilization of the adsorbates by intermolecular hydrogen bonding in SAMs with polar terminal groups.

A molecular brush model was presented to explain friction properties of various SAMs deposited on different substrates and with different backbone chains lengths, chain structures and end groups (Bhushan and Liu, 2001; Tambe and Bhushan, 2005b, g). Based on this model, during sliding, SAMs orient, which is responsible for low friction.
A comprehensive study to characterize the nanotribological properties of molecularly thick lubricant films was performed by Liu and Bhushan (2003a). A logarithmic increase in friction force with velocity was reported for some SAMs. However, beyond a certain critical velocity, the friction force value was seen to reach an equilibrium value.

1.3 Objectives of research work and organization of dissertation

The objective of the proposed research is to develop a fundamental understanding into the velocity dependent nature of nanoscale friction/stiction, adhesion and wear over a large range of sliding velocities that are of scientific as well as engineering significance and to extend the existing analytical models that are based primarily on scientific interpretations in order to encompass sliding velocity regimes of engineering importance. 

Figure 1.1 schematically illustrates the three primary tasks, the development of techniques, analytical formulations and experimental investigations, involved in conducting micro/nanotribological studies.

The challenging task of development of a technique for studying friction, adhesion and wear mechanisms on the nanoscale at very high sliding velocities is expected to provide the crucial breakthrough necessary for deriving a fundamental understanding of material behavior on the micro/nanoscale and to bridge the gap between science and engineering for studies pertaining to micro/nanostructures. Other capabilities developed in the research work such as nanofriction and nanowear mapping as well as material property mapping for identification of tribologically suitable materials for micro/nanoscale devices will not only bolster the results obtained from the proposed
studies and help extend the present understanding of material behavior, but will also branch new avenues in the design and development of nanotechnology applications.

Nanoscale friction, adhesion and wear studies at high sliding velocities

Figure 1.1: Primary tasks of the research work
Dissertation layout

The modifications made to a commercial AFM setup are discussed in detail in Chapter 2. Also discussed in this chapter are techniques for measuring friction and adhesion amongst other things; data collection methodologies and reproducibility and reliability issues. Micro/nanotribological studies and analytical formulations to understand velocity dependence of nanoscale friction, adhesion and wear are discussed in chapters 3 and 4. A scale dependence study performed to understand how friction and adhesion change from micro- to nanoscale is discussed in chapter 5. The last chapter discusses the major outcomes of the research work, the primary conclusions and impacts on design of nanotechnology applications.
CHAPTER 2
A NEW AFM BASED TECHNIQUE FOR HIGH SLIDING VELOCITIES

2 Need for speed: Extending the AFM capabilities for high sliding velocity studies

Extensive as the research efforts have been to characterize and understand the velocity dependence of friction (see Fig. 2.1), inherent instrument limitations on the highest sliding velocities achievable with the commercial AFM (<250 µm/s) have stymied research pursuits geared towards obtaining a fundamental understanding of failures resulting from high relative sliding velocities found in many real world applications (tens of mm/s to few m/s). Many MEMS/NEMS devices (some examples shown in Fig. 2.2) are designed to operate at very high rotational speeds ranging well above 100,000 rpm as in the case of micromotors (Bhushan 2004) and in some applications well above 1 million rpm such as for microgas turbines (Frechette et al., 2005). Given the size of these devices (the micromotor has a rotor diameter of 120µm), the relative sliding velocities that they operate at can reach several m/s. With the lack of sufficient experimental evidence, theoretical formulations have been limited to only low sliding velocity regimes. A study to investigate the velocity dependence of friction and adhesion for sliding velocity ranges of engineering importance would be crucial to the future design and development of micro/nano structures and devices for various nanotechnology applications.
Figure 2.1: Brief summary of research efforts to study velocity dependence of friction from atomic to micro/nanoscales over velocities ranging from a few nm/s to few mm/s (shaded area for ‘current research’ indicates unpublished results.)
Figure 2.2: Examples of nanotechnology applications that operate at high sliding velocities
2.1 **Modifications to the commercial AFM setup**

There are a number of commercial AFMs available on the market since 1989. Depending on the design of the AFM, i.e. whether the cantilever tip is scanned or the sample is scanned, AFMs can be broadly classified as large sample and small sample AFMs respectively (Bhushan, 1999a). Since the tip is held stationary in the small sample AFM, it provides better resolution and there is less noise contamination of the measured data, particularly for small scan sizes. However, a small sample AFM, as the name suggests, inherently requires the sample studied to be of small size and weight; else the piezo scanner operation is hindered. A large sample AFM provides the capability of studying larger samples and also provides an added flexibility needed for mounting samples on custom built stages for performing a wide array of studies. Goken et al. (1997), Hild et al. (1998) and Bobji and Bhushan (2001) modified the AFM setup by incorporating a tensile stage for in-situ imaging of thin films subject to tensile loading. Tambe and Bhushan (2004a) utilized a motorized stage for fatigue studies on thin films while Liu and Bhushan (2004) utilized a custom-built micropositioning stage for studying DMDs.

To achieve higher sliding velocities between the AFM cantilever tip and the sample surface, the primary approach has been to incorporate a customized stage that is capable of providing high sliding velocity. To date various techniques have been developed that modify the basic AFM setup in order to enhance its measurement capabilities and broaden the scope of tribological studies into higher sliding velocity regimes. One such approach has been to mount samples on a shear wave transducer and then driving it at very high frequencies (in the MHz range) (Yamanaka and Tomita, 1995;
Scherer et al., 1999; Marti and Krotil, 2001; Reinstadtler et al., 2003). The main challenges while modifying the AFM setup to achieve higher velocities are maintaining a constant velocity profile during the entire scan duration and at the same time scanning on larger surface areas to get a better understanding of nanotribological properties. In techniques employed by researchers using a shear wave transducer, the modulation amplitude was very small, in the nm range. Moreover friction force measurements as made by these researchers did not directly provide a fundamental understanding of nanoscale friction since they used a combination of oscillators, one to achieve high velocity and another for scanning. This does not provide a good estimate for nanoscale friction resulting from actual relative sliding between two components as oscillation of the tip (or the sample) while scanning changes the adhesive force at the tip sample interface and influences stick-slip behavior.

An alternative approach for accomplishing such a modification is using either a motorized stage or a piezo stage with large amplitude (~100 µm) and relatively low resonant frequency (few kHz). The most important parameters that need to be taken into consideration before implementing such modifications are the maximum travel (or scan size), the resolution, the accuracy and repeatability (hysteresis in forward and reverse scans), a constant velocity requirement over the entire scanning length, and the maximum sample size and weight allowable (this is particularly important for piezo stages). Motorized stages can prove to be relatively inferior to piezo stages due to vibration related issues, particularly in the direction perpendicular to the scanning axis (along the normal load axis of the cantilever tip). Such a stage can result in the cantilever tip being subjected to a constant change in normal load and the “chatter” can contaminate
measurements. Piezo stages provide better performance in this respect. However, the
disadvantage in using piezo stages is that they can be limited by the maximum travel, the
scanning frequency and the sample size. To achieve high velocities (in the tens of mm/s
range) using a piezo stage implies that both the scanning frequency and the scan size
should be relatively high. In most instances, however, there is a trade-off between the
maximum travel and the frequency of the piezo stage. Piezo stages can introduce
mechanical noise as a result of “ringing” which occurs because of poor piezo tracking.
Open loop operation (i.e. no active feedback) can result in the piezo losing its tracking
accuracy at high frequencies and thus the requirement of having a constant velocity over
entire scan length is not met. Instead therefore a closed loop operational mode can be
employed; however, this is generally at the expense of the maximum travel distance (scan
size) achievable.

2.2 A new piezo stage based AFM technique

Tambe and Bhushan (2005a) modified a commercial AFM setup (D3100,
Nanoscope IIIa controller, Digital Instruments, Santa Barbara, CA) by incorporating a
custom calibrated piezo stage (P621.1CL, HERA Nanopositioner with capacitive
feedback, Polytec PI, Karlsruhe, Germany). This piezo stage has an unloaded resonance
frequency of 800 Hz and a maximum scan length of 100 µm. The piezo stage drive units
are based on P-885 PICMA® low-voltage multilayer piezo ceramics, having an
extremely stiff friction-free flexure system with excellent guiding accuracy (small tilt
angles over the entire travel range). This design dispenses ultra-high power electronics
that can cause conventional piezo stacks to heat excessively when operated at high frequencies (Rego, 2003). Table 2.1 lists specifications of the piezo stage.

In the modified setup, the single axis piezo stage is oriented such that the scanning axis is perpendicular to the long axis of the AFM cantilever (this corresponds to the 90° scan angle mode of the commercial AFM). Scanning is achieved by providing a triangular voltage pulse to the piezo amplifier. Figure 2.3 (a) shows a schematic of the experimental setup and a cross-sectional schematic of the piezo stage. The piezo crystal drives the flexure and the sample mounted on top of it at the desired frequency, corresponding to the input voltage pulse. The displacement is monitored using an integrated capacitive feedback sensor, located diametrically opposite to the piezo crystal as shown in Fig. 2.3 (a). The capacitive sensor has a stationary target element mounted on the stage block and a moving probe element mounted on the flexure. The capacitance change, corresponding to the stage displacement, gives an indication of the amount of displacement. The stage can be operated in both open loop and closed loop operational modes. In the closed loop mode, the capacitive sensor signals are used as feedback by the piezo controller to provide better guiding and tracking accuracy. The closed loop position control of piezoelectric driven stages using capacitive feedback sensors provides linearity of motion better than 0.01 % with nanometer resolution and a stable drift free motion (Anonymous, 2003). Figure 2.3 (b) shows an operational flowchart for the piezo stage.

For scanning purposes, a triangular voltage pulse with 0-10V maximum peak-to-peak voltage is input to the piezo amplifier using a function generator. The triangular pulse gives constant displacement with respect to time and thereby ensures a constant scanning velocity, which is necessary during friction measurements. The input voltage pulse is fed
<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed loop travel</td>
<td>100 µm</td>
</tr>
<tr>
<td>Tilt (perpendicular to scan axis)</td>
<td>3 µrad</td>
</tr>
<tr>
<td>Closed loop linearity</td>
<td>0.01 %</td>
</tr>
<tr>
<td>Electrical capacitance</td>
<td>1.5 µF (±20%)</td>
</tr>
<tr>
<td>Stiffness</td>
<td>0.35 N/µm</td>
</tr>
<tr>
<td>Unloaded resonance frequency</td>
<td>800 Hz (±20%)</td>
</tr>
<tr>
<td>Maximum load</td>
<td>10 N</td>
</tr>
<tr>
<td>Resonance frequency @ 20g</td>
<td>520 Hz (±20%)</td>
</tr>
<tr>
<td>Lateral force limit</td>
<td>10 N</td>
</tr>
<tr>
<td>Operating temperature range</td>
<td>-40 to 120 °C</td>
</tr>
</tbody>
</table>

Table 2.1: Specifications of the P621.1CL piezo stage (Anonymous, 2003)
Figure 2.3: Schematic showing modifications done in the commercial AFM setup using the single axis piezo stage and a cross-sectional view showing constructional details of the piezo stage. The integrated capacitive sensors are used as feedback sensors to drive the piezo. The piezo stage is mounted on the standard motorized AFM base and operated using independent amplifier and controller units driven by a frequency generator (not shown in schematic). Operational flowchart showing the various components of stage operation (Tambe and Bhushan, 2005a)
Figure 2.3 continued
into the piezo amplifier and controller circuit where it was amplified to 0-100 V range and used for driving the piezo crystal. The piezo displacement is monitored by the capacitive sensor and in closed loop operational mode, is fed back to the controller.

The piezo stage displacements as measured by the capacitive sensors at two high frequencies in open and closed loop modes of operation are shown in Fig. 2.4. The open loop mode of operation (i.e. when no feedback was employed) had the advantage that piezo tracking was much better during the reversals in the direction of the stage motion while scanning, as is seen in Fig. 2.4. However, in the absence of active tracking, the piezo displacements stray away considerably from the input triangular profile. This is particularly evident at 250 Hz scan frequency when piezo “ringing”, high frequency noise, becomes a significant factor. The capacitive sensor can be used for providing feedback to piezo controller and this improves the piezo tracking considerably. In this case, the stage reversals are not linear and so stage velocity is not constant towards the ends when stage reverses direction. However, the tracking is significantly improved as a result of active feedback loop and this ensures that the velocity remains constant over most portion of the stage travel. Nonetheless the piezo does show hysteretic behavior for a 100 Hz scan frequency (Fig. 2.4). Hysteresis (area enclosed by the curve), is higher in the closed loop operational mode but this mode also gives a linear response over a large portion of the total scan length. The linear response implies a constant velocity and hence is more useful for friction force measurements.
Figure 2.4: Piezo stage displacements (in volts) as measured using the capacitive sensor for open loop and closed loop operation at 100 Hz and 250 Hz scanning frequencies; and piezo hysteresis under open and closed loop operational modes at 100 Hz scan frequency (Tambe and Bhushan, 2005a)
2.2.1 Friction force measurements using modified AFM setup

During the experiments the AFM cantilever was held stationary by maintaining a scan size of zero. The AFM controller feedback functioned in the conventional manner and maintained a constant normal load by adjusting the vertical deflection of the cantilever. As the mounted sample is scanned below the AFM tip, the torsional deflections of the tip are recorded by the photo-diode detector. The raw signals from the optical detection system are directly routed to a high speed data acquisition A/D board (National Instruments, NI PCI-6040E (PCI-MIO-16E-4), 12-bit, 16 Analog Input Multifunction DAQ). The photo-diode signals are a direct indication of the friction force encountered by the tip during sliding motion. The data acquisition system is synchronized to collect friction signals, with the input voltage pulse acting as the trigger. Raw friction data is processed using high sampling rates, up to 25 kilosamples/s/channel.

Figure 2.5 shows typical TMR signals collected on the commercial AFM setup and the modified AFM setup at two different scan frequencies on a scan size of 2 µm. TMR signals are the friction signals measured during the “trace” and “retrace” scans in an AFM. In case of the commercial AFM setup, noise sets in as a result of piezo “ringing” at high frequencies. Piezo ringing became evident beyond 30 Hz frequencies and it influenced the measurements more at higher scan frequencies. This noise often results in an underestimation of the friction force values. The friction data obtained using the modified AFM setup shows no piezo ringing even for high frequencies. The capacitive feedback loop maintains a constant velocity profile over the entire scan length. This ensures that the friction data obtained using the modified setup is the correct estimate of the friction resulting from the relative sliding between the tip and the sample.
Figure 2.5: Comparison of friction data measured for a scan size of 2 µm using the commercial and the modified AFM setup and comparison of friction force measurements conducted at different relative sliding velocities for single crystal silicon sample with native oxide using the commercial and the modified AFM setup (Tambe and Bhushan, 2005a)
even at high velocities. To eliminate any further discrepancies in the friction measurements that could result from any uncharacteristic behavior of the piezo stage during reversals, only the central portion of the TMR signals are considered while calculating the average values of friction.

Figure 2.5 also shows the actual friction force values calculated over a range of velocities using the commercial and the modified AFM setup. The values plotted are the average value of the TMR friction data over one scan cycle and each point on the graph was obtained by averaging data from at least ten such TMR cycles. Friction data obtained on a commercial AFM at high velocities (>100 µm/s) is not always reliable for reasons stated above and hence is not plotted. It is seen that the data obtained using the modified setup follows the same trend and the friction values are similar to those obtained with measurements done using the commercial AFM indicating that the data is highly reproducible. In the modified setup the piezo tracking error is seen to become significant for frequencies higher than 250 Hz and so for achieving higher sliding velocities larger scan sizes are used while studying the velocity dependence over the complete range of 1 µm/s to 10 mm/s.

2.2.2 Adhesive force measurements

The study of the adhesive force between the AFM tip and the sample surface is of significance because these forces can be considerably high on the micro/nanoscales, even comparable to the applied normal load. Measurements for adhesive force can be done in two different ways. Figure 2.6 shows the two ways using data obtained on a single crystal silicon Si (100) sample. Both methods yield similar values as seen from Fig 6 and this is
known from previous research (Liu and Bhushan, 2003a). In one method the friction force is measured for various normal loads and adhesive force is obtained from the negative intercept of the friction force vs. normal load curve on the normal load axis. The other method of calculating adhesive force is by using the ‘force calibration plot’ technique (Bhushan, 1999a). In this technique the force measurement starts with the sample far away and the cantilever in its rest position. The force curve, a plot of the cantilever deflection signals as a function of the voltage applied to the AFM piezo tube is obtained. A typical force curve obtained for Si (100) sample is shown in Fig 2.6. The arrows indicate the direction of piezo travel, or the advancement of the AFM tip towards the sample. Till point A there is no change in deflection signal as the AFM tip approaches the sample. At point A when the tip is few nanometers away from the sample surface the tip deflects due to attractive van der Waals forces. This marks the sharp drop from A to B. From point B as the AFM tip keeps advancing towards the sample the cantilever deflects under the load and this corresponds to the upward increase. After the maximum travel of the AFM piezo, it starts to retract, i.e. move away from the sample surface and we see a corresponding decrease in the cantilever deflection. At point C the normal load on the cantilever is fully relaxed. For further retraction of the piezo, however, the cantilever continues to remain in the deflected position and this continues till point D. This is because the tip remains stuck to the sample due to the adhesive force. Eventually the spring force of the cantilever overcomes the adhesive force and it snaps to its non-deflected, non-contact position. This corresponds to point E. The adhesive force can be calculated from the cantilever deflection and the spring constant. The cantilever deflection is the vertical distance between points D and E. In case of a relatively rigid
Figure 2.6: Two methods for calculating adhesive force. Slope of the friction force vs. normal load plot gives the coefficient of friction and the negative intercept on the normal load axis gives the adhesive force. Force calibration plot technique also gives adhesive force.
sample the horizontal distance C-E can also be used as the cantilever deflection since there is no deflection of the sample or it is negligible.

2.3 Closure

A new technique was developed to enable nanotribological investigations at high sliding velocities on materials, coatings and lubricants that find wide applications in MEMS/NEMS devices. The commercial AFM setup was modified with a custom calibrated nanopositioning stage capable of achieving high sliding velocities, up to 10 mm/s. An integrated capacitive sensor feedback system was employed for maintaining constant sliding velocities over the entire scan length. Using this new technique various nanotribological investigations can be performed for various materials, coatings and lubricants. The next chapter discusses studies conducted to understand the velocity dependence of friction, adhesion and wear. Also discussed are the effects of operating parameters such as rest time and acceleration on friction and adhesion. A comprehensive nanoscale friction model is developed to explain the velocity dependence.
3 Micro/nanoscale friction, adhesion and wear studies at high sliding velocities

3.1 Materials, coatings and lubricants for nanotechnology applications

Traditionally most micro/nanoscale devices have been primarily built using silicon as the structural material, not only owing to the well developed silicon micromachining technologies but also due to its good mechanical properties (Senturia, 2001; Madou, 2002; Bhushan, 2004). Despite its dominance though, many other structural materials are in use currently. Aluminum is used for micromirrors in the Digital Micromirror Device or DMD® (Hornbeck and Nelson, 1988; Hornbeck, 2001; Bhushan, 2004) and gold is used mainly as a reflective material for optical MEMS/NEMS, microswitches and microrelays (Bhushan, 2004). SiC, due to its excellent mechanical properties, thermal dissipative characteristics, chemical inertness and optical transparency, is particularly suited for applications involving harsh environments (Mehregany and Zorman, 1999; Sundararajan and Bhushan, 1998). Diamond and the hard amorphous carbon coatings, commonly called diamondlike carbon or DLC exhibit low friction and wear and are potential materials for various industrial applications (Grill 1997; Bhushan, 1999c).
These materials pose a serious challenge though in making devices with moving parts owing to their inherent high stiffness. Also it is not clear whether they should be the first choice materials for applications in biology and chemistry that require fluidic control (Quake and Scherer, 2000). Intensive research, focused on exploring fluid applications, has led to the introduction of alternative polymeric materials and their related fabrication technologies (Tang and Lee, 2001; McDonald and Whitesides, 2002). The wide range of available polymer materials allows manufacturers to choose materials’ properties suitable for their specific application (Quake and Scherer, 2000; Becker and Locascio, 2002; Bhushan, 2004).

Not all metal/polymer materials or coatings are suitable for all nanotechnology applications though and material selection is strongly governed by the operating and environmental parameters that the micro/nano structures and devices are designed to work in. The efficiency, power output and steady state operation of micro/nano structures and devices can be critically influenced by adhesion, friction and wear (Maboudian and Howe, 1997; Bhushan 1998, 2003, 2004; Liu and Bhushan, 2004). This has necessitated the application of low friction and low adhesion ultra-thin lubricant films for the protection of contacting surfaces in micro/nano structures. One of the lubricant systems for this purpose is SAMs, monomolecular thick films deposited on solid substrates. SAMs consist of three building groups: a head group that reacts with a substrate, a tail group that interacts with the outer surface of the film and a spacer (backbone) chain group that connects the head and tail groups (Ulman, 1991, 1996). The appropriate choice of the three groups will contribute to the optimal design of the SAMs. Commercially used DMDs are coated using a self-assembled monolayer of perfluorinated n-alkanoic acid
(CₙF₂n₋₁O₂H) by a vapor phase deposition process (Hornbeck, 1997; Wallace et al., 1996; Henck, 1997; Lee et al., 1999, 2000; Gudeman, 2001; Robbins and Jacobs, 2001).

3.2 Understanding normal load and velocity dependence of friction force: Nanoscale friction mapping

Contrary to classical friction laws postulated by Amontons and Coulomb centuries ago, nanoscale friction force is found to be strongly dependent on the normal load and sliding velocity. Many materials, coatings and lubricants show reversals in friction behavior on the micro/nanoscale corresponding to transitions between different friction mechanisms (Riedo et al., 2003; Liu and Bhushan, 2002, 2003a; Gnecco et al., 2004; Tambe and Bhushan, 2004b, 2005a-i). A fundamental understanding of normal load and velocity dependence of nanoscale friction is of paramount importance, not only for the design of reliable industrial and scientific applications but also to provide a bridge between science and engineering on the micro/nanoscale.

Tambe and Bhushan (2005i) have studied nanoscale friction as a function of normal load and sliding velocity and used a novel mapping technique that helps identify, demarcate and classify different friction mechanisms. Figure 3.1 shows the nanoscale friction maps obtained to study the friction force dependence on normal load and sliding velocity for single crystal silicon with native oxide layer (Si (100)), highly oriented pyrolytic graphite (HOPG), DLC, aluminum (Al) and polymers polydimethylsiloxane (PDMS) and polymethylmethacrylate (PMMA). Table 3.1 lists the materials used in this study along with brief descriptions/preparation details. Experiments were conducted with the modified AFM setup (Tambe and Bhushan, 2005a). Measurements were performed
<table>
<thead>
<tr>
<th>Material</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (100)</td>
<td>Wafer World Inc. (West Palm Beach, Florida, USA)</td>
</tr>
<tr>
<td>DLC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Filtered cathodic arc deposition on Si (100) substrate, 10 nm thick film</td>
</tr>
<tr>
<td>Al&lt;sup&gt;b&lt;/sup&gt;</td>
<td>250 nm thick Al alloy film on Si substrate (film consists of an alloy with &gt;90% Al and traces of Ti and Si)</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10% by weight of PMMA dissolved in an organic solvent (anisole) is spin coated on a glass substrate, 1-2 µm thick film</td>
</tr>
<tr>
<td>PDMS&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Mixture of a translucent base in a curing agent (10:1 ratio) is vacuum dried and cured for 48 hrs at room temperature</td>
</tr>
<tr>
<td>HDT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>24 h immersion of Au (111)/Si (100) substrates in 1 mM HDT solution in ethanol, 1.89 nm thick film</td>
</tr>
<tr>
<td>Z-15&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2-3 nm thick film deposited on Si (100) substrate by dip coating technique</td>
</tr>
<tr>
<td>Z-DOL&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2-3 nm thick film deposited on Si (100) substrate by dip coating technique</td>
</tr>
</tbody>
</table>

<sup>a</sup> Liu and Bhushan (2003a)  
<sup>b</sup> Wei et al. (2004)  
<sup>c</sup> Bhushan and Burton (2004)  
<sup>d</sup> Liu and Bhushan (2003b)

Table 3.1: Brief description of sample preparation
Figure 3.1: Contour maps showing friction force dependence on normal load and sliding velocity and summary of characteristic contour patterns and their significance (Tambe and Bhushan, 2005i)
using square pyramidal Si$_3$N$_4$ tips with nominal radii 30-50 nm, mounted on gold coated triangular Si$_3$N$_4$ cantilevers having a nominal spring stiffness of 0.32 and 0.58 N/m. Experiments were performed over a range of velocities from 5 µm/s to 1 mm/s and in controlled environment of 20±2 °C and 50±5 % relative humidity. A scan size of 2 µm was used for friction measurements.

The contour maps were generated from friction force data collected at different normal loads and sliding velocities. The contours represent constant friction force lines and are marked by the value of the friction force in nN. The contours for each material are characteristic of the friction behavior exhibited by that particular material even though there are some features that can be classified as universal irrespective of the material and are discussed next. Based on the specific arrangement of contour lines, the dominant friction mechanisms can be identified. At the bottom half of Fig. 3.1 the most commonly observed features in the contours (or the characteristic contours) as found from our study are summarized and the significance of each is stated.

Horizontal contour lines indicate the velocity independent nature of friction force. This behavior is found at high velocities for HOPG, at moderately high velocities for Al and at low velocities for PMMA. Studies on the nanoscale friction force dependence on velocity (Riedo et al., 2003) indicate that friction force becomes constant relative to sliding velocity when the atomic scale stick-slip occurring at low sliding velocities loses its dominance. A constant friction force with respect to sliding velocity would appear as horizontal contour on a friction map and is the reason for example for the horizontal contours seen for HOPG at high velocities. Vertical contour lines indicate a normal load independence of friction force. In all the samples studied this behavior is not seen,
although the steep contour lines for Si (100), HOPG and Al indicate that there is a very small normal load dependence on friction at low velocities. For all practical instances it would be impossible to find a material that shows normal load independence of friction force.

Some other characteristic contours are those with slanting lines with either a positive or negative slope. These friction contours arise from the microscale stick-slip related contributions or from the formation of meniscus bridges by preferential condensation of liquid films at the sliding interface, particularly for hydrophilic interfaces. Researchers have shown that friction force increases with velocity due to atomic scale stick-slip (Riedo et al., 2003; Gnecco et al., 2004). On a friction map, this increase would be seen as slanted contours with a positive slope, i.e. an increase in friction force as one moves from left to right on the map. In this study, HOPG, DLC and Al showed this behavior. Stick-slip can also originate as a result of other mechanisms and result in a decrease in friction force with an increase in sliding velocity (Ruths et al., 2004). This behavior would result in slanted contours with a negative slope on the friction map such as seen for PMMA at high sliding velocities and for PDMS. The friction force arising from meniscus contributions, found for hydrophilic surfaces such as Si(100), results in the drop in friction force with an increase in sliding velocity. A minimum threshold equilibrium time is necessary for the formation of stable meniscus bridges at contacting and near-contacting asperities for a sliding interface (Bouquet et al., 1998; Tambe and Bhushan, 2005b). With increasing velocity less number of meniscus bridges build-up at the interface and thus the overall contribution to friction force drops
with an increase in velocity. This behavior would manifest itself in the form of slanted contour lines with negative slope on the friction map.

Contour maps can also consist of concentric contour lines. DLC appears to show this kind of behavior. Concentric contour map implies a peak friction force corresponding to a critical normal load and sliding velocity. Beyond that point any further increase in either the normal load or the sliding velocity would result in a decrease in the friction force. This kind of behavior typically would imply a phase transformation by formation of a low friction phase at the interface or localized melting at the contact zone. Phase transformation has been known to occur for DLC resulting in a low friction graphite-like layer by a sp\(^3\) to sp\(^2\) phase transition (Grill, 1997; Tambe and Bhushan, 2005e). Localized melting would arise from very high frictional energy dissipation and is expected particularly in case of polymer materials. In this study, PMMA appeared to show concentric lines at moderately high velocities, however for the given range of normal load and sliding velocity, the experimental evidence is not sufficient to support this hypothesis.

Another characteristic contour is the one where contour lines change direction suddenly. This implies a sudden change in the dominant friction mechanism. Si(100) and PMMA showed such behavior. In case of silicon, researchers have reported formation of a Si(OH)\(_4\) layer at the sliding interface at high sliding velocities (Mizuhara and Hsu, 1992). It is believed, based on the contour maps, that this effect is initiated at a particular sliding velocity and that this is the reason for the sudden change in friction force. For Si(100), meniscus contribution to friction force is also a dominant mechanism; however
both these mechanisms are known to co-exist in tandem and result in a decrease in friction force with velocity (Liu and Bhushan, 2003a).

3.3 **Velocity dependence of friction and adhesion**

Various researchers have investigated the dominant friction mechanisms on the micro/nanoscale and presented analytical models to corroborate their studies (Chilamakuri and Bhushan, 1999; Gnecco et al., 2000, 2004; Riedo et al., 2002, 2003; Bhushan, 2003). Most of these models have however remained limited in their focus and researchers are left short handed when trying to explain friction behavior scaling multiple regimes. The nanoscale friction maps provide fundamental insights into the friction force dependence on normal load and sliding velocity. They help identify and classify the dominant friction mechanisms as well as determine the critical operating parameters that influence transitions between different mechanisms. The new AFM based technique developed by Tambe and Bhushan (2005a) promises high sliding velocities while enabling friction measurements over large scan sizes and gives a direct measure of friction. It is ideal for investigating friction mechanisms at different sliding velocities (up to 10 mm/s) and developing a comprehensive analytical model to explain the velocity dependence of nanoscale friction for both dry (unlubricated) and lubricated interfaces with both hydrophilic and hydrophobic properties and studying the transitions between different friction mechanisms.

Velocity dependence of friction was studied for various samples that were selected so as to include dry (unlubricated) and lubricated interfaces with hydrophilic and hydrophobic properties (Tambe and Bhushan, 2005b). Experiments were conducted on
single crystal silicon (Si (100) with native oxide layer), 10 nm thick DLC films, a SAM of hexadecanethiol (HDT), and Z-15, a typical perfluoropolyether (PFPE) lubricant with non-polar –CF₃ terminal end groups. The detailed procedures and preparation techniques of these thin films are given in following references: DLC in Bhushan (1999c) and Liu and Bhushan (2003b), HDT in Liu and Bhushan (2003b) and Bhushan and Liu (2001) and Z-15 in Liu and Bhushan (2003a). Table 3.2 lists the samples used in these studies and the nature of the sliding interface. Experiments were conducted using square pyramidal Si₃N₄ tips, with a nominal radius of 30-50 nm, mounted on gold coated triangular Si₃N₄ cantilevers with spring constants of 0.58 N/m. The friction force measurements were conducted over a range of velocities, between 1 µm/s and 10 mm/s, for scan sizes of 25 µm and at a constant normal load of 70 nN. The adhesive force measurements were performed over 2 µm scan sizes. All measurements were conducted in controlled environment of 20±2 °C and 50±5 % RH. The friction measurements at each velocity were carried out on different locations on the samples to prevent any bias in the measurements.

Figure 3.2 gives the velocity dependence of friction force for the samples studied, over a wide range of velocities from few µm/s to 10 mm/s. For Si (100) with a native oxide layer and Z-15, the friction force was found to initially decrease with velocity, reach minima, and then start to increase with velocity. The initial decrease is logarithmic and has been known to result from diminishing meniscus force contributions to the overall friction force with velocity (Bhushan, 2003; Koinkar and Bhushan, 1996; Liu and Bhushan, 2003a; Tambe and Bhushan, 2004b, 2005b). For the hydrophilic Si (100) sample, the meniscus force contribution arises from condensed water molecules,
<table>
<thead>
<tr>
<th>Surface</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (100)</td>
<td>Solid, dry (unlubricated), hydrophilic surface</td>
</tr>
<tr>
<td>DLC</td>
<td>Solid, dry (unlubricated), partially hydrophobic surface</td>
</tr>
<tr>
<td>HDT</td>
<td>Molecularly thick, lubricated, partially hydrophobic surface</td>
</tr>
<tr>
<td>Z-15</td>
<td>Liquid, lubricated, Z-15 surface with condensed water molecules</td>
</tr>
</tbody>
</table>

Table 3.2: Surface characteristics of samples used for velocity dependence studies.

while for Z-15, menisci contribution arises from the Z-15 molecules as well as the condensed water molecules. Beyond a certain critical velocity, the residence time of the tip at the sample surface is not sufficient to form meniscus bridges and the meniscus force contribution to the friction force drops out. Koinkar and Bhushan (1996) have suggested that in the case of samples with mobile films, such as condensed water and Z-15 films, alignment of liquid molecules (shear thinning) is responsible for the drop of friction force with an increase in scanning velocity. This could be another reason for the decrease in friction force for Si (100) and Z-15 films.

Unlike the results obtained for Si (100), experiments run on the DLC sample show an initial logarithmic increase in friction force followed by a near logarithmic decrease with velocity. The DLC film is partially hydrophobic and can absorb only a few water molecules in ambient conditions (Liu and Bhushan, 2003b; Tambe and Bhushan, 2004b). Surprisingly and interestingly, beyond a critical velocity, the friction force is
Figure 3.2: Velocity dependence of friction force measured using a Si$_3$N$_4$ tip of 30-50 nm tip radius at a normal load of 70 nN and for velocities ranging between 1 µm/s and 10 mm/s at 20±2 °C and 50±5 % RH for Si (100), DLC, HDT, Z-DOL, Z-15, PMMA and PDMS.
found to drop nearly logarithmically with any further increase in velocity. The decrease in friction force is the result of phase transformation of the sample surface due to higher energy dissipation from high velocity impacts (Tambe and Bhushan, 2005e). These findings are discussed in more details in a later section. In the case of HDT, the friction force is seen to increase with velocity over the entire range of velocities studied. Similar increase has been reported before at lower velocities by Liu and Bhushan (2003a). However they observed different behavior at higher normal loads and instead found that the friction force initially increases linearly with velocity and then reaches a plateau after a certain critical velocity. This trend is believed to be followed even for lower normal loads but the transition is not so distinct. Moreover the increase is believed to have not a logarithmic trend but instead a linear trend for all normal loads.

For friction experiments conducted at high sliding velocities tip/sample wear can be a critical issue and can influence friction measurements. It is known that continuous sliding, high normal loads and sliding velocities can all result in considerable tip wear. Tambe and Bhushan (2005c) have studied the influence of these factors on sample and tip wear by measuring friction force as a function of number of sliding distance at different loads and sliding velocities for various samples including those used in this study. They found that the friction force remains fairly constant over a large number of sliding cycles (up to 50,000) after which there is a sudden change in friction force. In their experiments, the tip radius was found to have increased from the nominal value of 30-50 nm to as high as 60-70 nm. Further studies to understand wear of sample surface (Tambe and Bhushan, 2005h) indicate that no visible wear is expected to occur for the operating parameters that
were selected in this study in which all the experiments were terminated much before 500 sliding cycles. The results obtained from the wear studies are discussed in details later.

Figure 3.3 give the velocity dependence of the adhesive force for the samples studied. Adhesive force measurements were made on a smaller scan size of 2 µm, and over a velocity range from few µm/s to 1 mm/s. Measurements done on larger scan size of 25 µm did not yield consistent and reproducible results for Si (100) and HDT. Instead therefore, the “force calibration plot” technique (Bhushan, 1999a) was employed to measure the adhesive force after each high velocity (10 mm/s) experiment and the values obtained from these tests are plotted in the Figs. 3.3. The Figs 3.3 also give the static adhesive force values measured by the FCP technique before the high velocity experiments. For Si (100), the adhesive force was found to remain fairly constant initially, then increase rapidly and later drop again at very high velocity, whereas for Z-15 it rapidly decreases and then remains almost constant. The increase in adhesive force for Si (100) is believed to be the result of a tribochemical reaction at the tip-sample interface, in which a low shear strength Si(OH)$_4$ layer is formed (Mizuhara and Hsu, 1992; Liu and Bhushan, 2003a). This layer gets replenished continuously during sliding and results in a higher adhesive force between the tip and sample surface. For Z-15, with no meniscus contributions, the adhesive force decreases at high velocities. For DLC and HDT, the adhesive force is constant initially but then starts increasing. The increase is rapid beyond a critical velocity and is believed to be the result of phase transformation by formation of a low shear strength layer at the tip sample interface in case of DLC (Grill, 1997; Tambe and Bhushan, 2005e) and higher pull-off forces exerted by the SAM molecules as a result of viscous drag on the tip at high
Figure 3.3: Velocity dependence of adhesive force measured using a Si$_3$N$_4$ tip of 30-50 nm tip radius at a normal load of 70 nN and for velocities ranging between 1 µm/s and 10 mm/s at $20\pm 2$ °C and $50\pm 5$ % RH for Si (100), DLC, HDT, Z-DOL, Z-15, PMMA and PDMS
velocity in case of HDT (Clear and Nealey, 2001). These results and the interpretations for each sample are discussed in detail in the next section.

### 3.4 Origins of nanoscale friction

#### 3.4.1 Comprehensive model for nanoscale friction

Tambe and Bhushan (2005b) have developed a comprehensive friction model starting from the classical theory of friction (Bowden and Tabor, 1950, 1964, 1973; Singer and Pollock, 1992; Bhushan, 1999b) by identifying the primary sources of nanoscale friction. The nanoscale friction force between two contacting surfaces is a result of three components — interfacial adhesion between contacting asperities, energy required for deformation of contacting asperities during relative motion, and stick-slip. The stick-slip effect can arise on both atomic and micro/nanoscales and is known to be velocity dependent (Bowden and Tabor, 1973; Mate et. al, 1987; Bouhacina et al., 1997; Bhushan, 1999a; Gnecco et al., 2000; Bennewitz et al., 2001; Riedo et al., 2003; Ruths et al., 2004). Assuming negligible interaction between the adhesion and deformation processes and the stick-slip during sliding, we can add them (Bhushan, 1999b). The total friction force, $F$, is therefore,

$$ F = F_{adh} + F_{def} + F_{stick-slip} $$

(3.1)

where, $F_{adh}$ = friction force due to adhesive interaction at the contacting surfaces

$F_{def}$ = friction force due to deformation at the interface of contacting surfaces

$F_{stick-slip}$ = friction force due to stick-slip between contacting surfaces

Each of these three contributing factors is considered and the velocity dependence of each of them is investigated in detail below.
3.4.1.1 Adhesion contribution to friction force

When two nominally flat surfaces are placed in contact under certain normal load, the contact takes place at the asperity peaks, the load being supported by the deformation of the contacting asperities; and discrete contact spots are formed. The proximity of the asperities results in adhesive contacts caused either by physical or chemical interaction. When these surfaces move relative to each other, a lateral force is required to shear the adhesive bonds formed at the interface (Bhushan, 1999b). From the classical theory of adhesion, to a very rough first approximation, the adhesive friction force, $F_{adh}$, for two contacting surfaces having real area of contact, $A_r$, and relative sliding velocity $V$, is defined as below (Bowden and Tabor, 1950)

$$F_{adh} = A_r \left( \alpha \tau_\alpha + (1 - \alpha) \tau_l \right)$$

$$= A_r \left( \alpha \tau_\alpha + (1 - \alpha) \frac{\eta_l V}{h} \right)$$  \hspace{1cm} (3.2)

where, $\alpha$ = fraction of dry contact ($0 \leq \alpha \leq 1$)

$\tau_\alpha$ = average shear strength of dry contact

$\tau_l$ = average shear strength of liquid (water or lubricant) film

$\eta_l$ = viscosity of liquid (water or lubricant) film

$h$ = thickness of liquid (water or lubricant) film

The contacts at the asperities can be either elastic or plastic, depending primarily on the surface roughness and mechanical properties of the mating surfaces (and on velocity as shown later). The real area of contact is therefore given by following equations (Bhushan, 1999b)
For elastic contacts, \( A_r \sim \frac{3.2 F_N R_p^{1/2}}{E^* \sigma_p^{1/2}} \), and for plastic contacts, \( A_r \sim \frac{F_N}{H} \) (3.3)

where, \( F_N \) = total normal load (normal load of tip + meniscus forces, if any)

\( E^* \) = composite Young’s modulus for the two surfaces in contact

\( R_p \) = radius (average value) of asperity peaks

\( \sigma_p \) = standard deviation of asperity peak heights

\( H \) = hardness of softer sample

With the presence of a thin liquid film such as lubricant or adsorbed water layer at the contact interface, menisci form around the contacting and near contacting asperities due to surface energy effects. The attractive meniscus force arises from the negative Laplace pressure inside the curved menisci and is given by the product of this pressure difference and the immersed surface area of the asperity. This intrinsic attractive force may result in high friction and wear. For nanoscale contacts the meniscus force contribution, \( F_m \), becomes comparable to the normal load, \( W \), (Bhushan, 2003) and so the total normal load can be written as

\[
F_N = W + F_m
\]

(3.4)

The total meniscus force at the sliding interface is obtained by summing up the meniscus forces from all individual contacting and non-contacting asperities where menisci are formed (Bhushan, 2003) and is given by the expression

\[
F_m = 2\pi R_t \gamma (\cos(\theta_1) + \cos(\theta_2)) N(t)
\]

(3.5)

where, \( R_t \) = radius of the contacting tip

\( \gamma \) = surface tension of the liquid film

\( \theta_1 \) and \( \theta_2 \) = contact angles for the sample and the tip
\[ N(t) = \text{number of contacting and near contacting asperities where menisci build up and is a function of the rest time (residence time) of the tip at the sliding interface) } \]

Chilamakuri and Bhushan (1999) proposed a kinetic meniscus model to determine meniscus force as a function of time. This model considers liquid flow towards the contact zone until equilibrium is attained. The driving forces for such a flow are the Laplace or capillary pressure, which is the pressure gradient due to the curved liquid-air interface, and the disjoining pressure, which is the force per unit area that the molecules on the surface of a liquid film experience relative to that experienced by the molecules on the surface of the bulk liquid. This model is particularly developed for a liquid film and it takes into consideration only those asperities which are fully immersed while estimating the total meniscus force. Meniscus bridge formation is, however, not restricted to interfaces that are fully immersed in a liquid film. Meniscus bridges can form by condensation of liquid at preferential interstitial locations. An alternate approach to modeling meniscus bridge formation is the one based on the thermal activation process (Bocquet et al., 1998). The meniscus bridge formation is assumed to be the result of preferential condensation of liquid at the interface by overcoming an energy barrier that is required for the coating films to fully grow and coalesce and form menisci at the interface. The expression for the total number of asperities where meniscus bridges are formed is derived starting from the Kelvin relation and by determining the total energy required for nucleating meniscus bridges by condensation of a certain volume of water (Evans, 1989) at the tip-sample interface.
The spatial extent of a meniscus bridge is controlled by the radius of curvature, \( r_{\text{eq}} \), of the liquid interface, which, at the liquid-vapor equilibrium, is fixed by the Kelvin relation (Evans, 1989)

\[
\frac{1}{r_{\text{eq}}} = \frac{\rho k_B T}{\gamma} \ln \left( \frac{p_s}{p} \right)
\]

(3.6)

where, \( \rho \) = density of the liquid,

\( k_B \) = Boltzmann constant,

\( T \) = absolute ambient temperature, and

\( p_s/p \) = ratio of ambient pressure to the saturation pressure at that corresponding ambient temperature (equal to relative humidity).

Under ambient conditions, this expression yields a value of \( r_{\text{eq}} \) of nanometer dimensions, thereby implying that liquid bridges are able to form only in nanometer-scale interstitial locations. For two surfaces in close contact with asperity spacing less than a critical distance of the order of the Kelvin radius, \( r_{\text{eq}} \), capillary condensation should occur (Evans, 1989). However, an energy barrier has to be overcome, as the coating films have to grow and coalesce in order to fill the gap between the surfaces. Along this path, the free energy of the system increases to a maximum as the films are about to merge. The energy barrier is therefore the free energy required for condensing a certain water volume from the corresponding undersaturated vapor phase (Bocquet et al., 1998) and is given by the expression

\[
\Delta E(e) = \frac{1}{r_{\text{eq}}} \gamma v_i = \frac{\rho k_B T}{\gamma} \ln \left( \frac{p_s}{p} \right) v_i
\]

(3.7)

where, \( v_i \) = liquid volume needed to nucleate the liquid bridge.
For a meniscus bridge with cross-sectional area $A$, and spacing, $e$, between the surfaces at the nucleating site, the expression for the free threshold energy becomes

$$\Delta E(e) = \rho k_B T \ln \left( \frac{p_s}{p} \right) eA$$  \hspace{1cm} (3.8)

Assuming a thermal activation process, the number of menisci bridges forming at the contacting and near-contacting asperities will increase with rest time (or residence time of the tip at the sample surface during sliding) (see Fig. 3.4) (Bocquet et al., 1998) and is given by

$$t(e) = t_a \exp(\Delta E(e)/k_B T)$$ \hspace{1cm} (3.9)

where $t_a$ = condensation time for one liquid monolayer. From eqs. (3.8) and (3.9), the maximum spacing, $e_{\text{max}}$, to which a meniscus bridge can build in a given time, $t$, is therefore given by

$$e_{\text{max}}(t) = \frac{1}{A\rho} \frac{1}{\ln \left( \frac{p_s}{p} \right)} \ln \left( \frac{t}{t_a} \right)$$ \hspace{1cm} (3.10)

For the near contacting asperities, menisci bridges will not form if their spacing is greater than $e_{\text{max}}$, for the given residence time. Thus the number of meniscus bridges forming at the tip-sample interface will depend on the peak height distribution. Based on the statistical height distribution, the total number of contacting and near-contacting asperities that contribute towards the total meniscus force can be approximated based on the typical width of the distribution of distances between the surfaces, $\lambda$ (Bocquet et al., 1998; Riedo et al., 2002). The expression for $N(t)$ can therefore be given by
Figure 3.4: Schematic showing meniscus bridge formation at contacting and near contacting asperities. Menisci bridges cannot be formed at near contacting asperities if the spacing, \( e \), is greater than maximum spacing \( e_{\text{max}} \), corresponding a particular given residence time of the tip at the tip-sample interface (Tambe and Bhushan, 2005b).
\[ N(t) = \frac{e_{\text{max}}}{\lambda} = \frac{1}{\lambda A \rho} \frac{1}{\ln \left( \frac{p_s}{p} \right)} \ln \left( \frac{t}{t_a} \right) \]

\[ = \frac{1}{\lambda A \rho} \frac{1}{\ln \left( \frac{p_s}{p} \right)} \ln \left( \frac{V_a}{V} \right) \]  \hspace{1cm} (3.11)

where, \( V_a \) = critical velocity corresponding to the condensation time of one liquid monolayer.

Substituting eq. (3.11) in eq. (3.5) we get,

\[ F_m = \frac{2 \pi R \gamma (\cos(\theta_1) + \cos(\theta_2))}{\lambda A \rho \ln \left( \frac{p_s}{p} \right)} \ln \left( \frac{V}{V_a} \right) = -\phi_m R_i \ln \left( \frac{V}{V_a} \right) \]  \hspace{1cm} (3.12)

where, \( \phi_m = \frac{2 \pi \gamma (\cos(\theta_1) + \cos(\theta_2))}{\lambda A \rho \ln \left( \frac{p_s}{p} \right)} \)  \hspace{1cm} (3.13)

Then from eqs. (3.2), (3.3), (3.4) and (3.12) we have

\[ F_{\text{adh}} = \phi_{\text{adh}} \left( W - \phi_m R_i \ln \left( \frac{V}{V_a} \right) \left( \alpha \tau_a + (1-\alpha) \frac{\eta V}{h} \right) \right) \]  \hspace{1cm} (3.14)

where, \( \phi_{\text{adh}} = \frac{3.2 R_p^{1/2}}{E^* \sigma_p^{1/2}} \) for elastic contacts and \( \phi_{\text{adh}} = \frac{1}{H} \) for plastic contacts.

As velocity increases the time available for stable menisci formation reduces and so menisci do not form at all of the contacting or near-contacting asperities at the tip-sample interface. The maximum height that a meniscus bridge can build up to decreases logarithmically with increasing sliding velocity (as is evident from eq. (3.10)). Moreover the contribution of viscous shearing of the water film, at contacting and near contacting asperities where menisci are formed, to the adhesive friction force is very small and can be neglected in most instances (Bhushan, 1999b). For such a case eq. (3.14) reduces to
\[ F_{\text{adh}} \sim \mu_{\text{adh}} \left( W - \phi_m R_i \ln \left( \frac{V}{V_a} \right) \right) \]

where, \( \mu_{\text{adh}} = \phi_{\text{adh}} (\alpha \tau) \)  

As \( V \) approaches \( V_a \), the meniscus contribution decreases and friction force drops, until at a critical velocity \( V=V_a \), when the sliding velocity is too high for stable menisci to form anywhere at the interface and this is when the friction force levels off. At this point the adhesive friction force contribution to the overall friction force diminishes and friction is now dominated only by deformation related friction force and stick-slip.

In our experiments meniscus force contribution needs to be considered for Si (100) and Z-15 samples. In case of Si (100), the meniscus force contribution is solely the result of condensed water molecules and eq. (3.15) holds. For Z-15, however, meniscus force contribution arises from condensed water molecules as well as the liquid Z-15 film itself. For such a case a combination of both the kinetic meniscus model suggested by Chilamakuri and Bhushan (1999) and the thermal activation model suggested by Bouquet et al. (1998) and Riedo et al. (2002) needs to be taken into consideration while determining the velocity dependence of friction force. Both these models however predict a logarithmic decrease in friction force with velocity. From our results we find that the friction force decreases logarithmically with velocity and follows eq. (3.15) pretty closely for both Si (100) and Z-15 samples.

### 3.4.1.2 Asperity deformation contribution to friction force

Now, we address the second contributing component of the nanoscale friction that results from energy dissipation due to deformation of the contacting asperities (see Fig. 3.4.1.2).
Figure 3.5: Schematic of multiasperity interaction at the AFM tip-sample interface resulting from asperity impacts. The normal load is $W$, tip radius is $R_t$ and for a hemispherical asperity of radius, $R$, the impact results in a deformation zone of diameter $a$ and height $z$ (Tambe and Bhushan, 2005b)
During any relative motion, adhesion and asperity interactions are always present. Their contribution, though, may or may not be significant and depends on surface roughness, relative hardness of the two surfaces in contact, the normal load and sliding velocity. Low sliding velocity means less energy is available for deformation. As the relative sliding velocity increases, the impacts between surface asperities result in more and more energy dissipation and the deformation related friction force is given by

$$F_{df} = \frac{\text{work done (frictional energy dissipated)}}{\text{sliding distance over which energy is expended}}$$

= (force to deform one asperity)(number of asperities deformed) \hspace{1cm} (3.16)

We derive a relation between sliding velocity and the deformation related friction force, starting from the Archard equation for wear of asperities of contacting surfaces. The amount of area worn away depends on the roughness of the sample surfaces, the sliding velocity (energy available from the relative sliding motion) and the relative hardness of the contacting surfaces. For a surface with random peak height distribution, \(\phi(z)\), and \(N_0\) number of peaks in the nominal contact area, the total force corresponding to the energy dissipated during deformation of asperities can be written as (Bhushan, 1999b)

$$F_{df} = \int_0^{z_0} \left[ \pi a^2 H \right] N_0 \phi(z) dz \hspace{1cm} \text{for plastic contacts}$$

and,

$$F_{df} = \int_0^{z_0} \left[ \pi a^2 E^* \left( \frac{\sigma_p}{R_p} \right)^{1/2} \right] N_0 \phi(z) dz \hspace{1cm} \text{for elastic contacts} \hspace{1cm} (3.17)$$

where, \(z_0=\text{maximum nominal depth over which wear can occur for given sliding velocity}\)

Now consider a single asperity interaction at the tip-sample interface as illustrated in Fig. 3.5. Assuming the profile of the asperity on the sample surface to be
hemispherical, we then have for the two surfaces moving with relative sliding velocity \( V \), a wear depth of \( z \) and worn area of diameter \( a \). The rate of wear depth is given by (Bhushan, 1999b),

\[ z = \frac{kF_NV}{\pi a^2 H} \quad \text{for plastic contacts and,} \]
\[ z = \frac{kF_NV}{\pi a^2 E^* \left( \frac{\sigma_p}{R_p} \right)^{1/2}} \quad \text{for elastic contacts} \quad (3.18) \]

where, \( k = \) non dimensional wear coefficient that depends on the materials in contact

Substituting eq. (3.18) in eq. (3.17) we obtain

\[ F_{\text{def}} = \int_0^{\int_0^{\infty}} kF_NV \frac{1}{z} \phi(z) dz \]
\[ = kF_NV N_0 \int_0^{\infty} \frac{1}{z} \phi(z) dz \quad (3.19) \]

Assuming the rate of wear depth, \( \dot{z} \), to be a constant with respect to the actual wear depth, \( z \), we can factor out the term \( 1/z \) from the integral.

For Gaussian distribution of peak heights, we need to use numerical methods to evaluate the integral. A simpler relation can be obtained for \( F_{\text{def}} \) by assuming the peak height distribution to have an exponential distribution, \( \phi(z) = \exp(-z) \)

Thus eq. (3.19) becomes,

\[ F_{\text{def}} = \frac{kF_NV N_0}{\dot{z}} \int_0^{\infty} \exp(-z) dz \]
\[ = \frac{\pi kF_NV N_0}{\dot{z}} \left( 1 - \exp(-z_0) \right) \quad (3.20) \]
From Fig. 3.5, for a hemispherical asperity of radius, R, and diameter of worn area, \( a_0 \), corresponding to maximum wear, we have, the maximum wear depth, \( z_0 = a_0^2 / 8R \).

The diameter of the worn asperity depends on the relative hardness of the contacting surfaces, the normal load and the sliding velocity.

Substituting in eq. (3.20) we get,

\[
F_{def} = \frac{\pi kF_aVN_o}{z} \left( 1 - \exp\left(-\frac{a_0^2}{8R}\right) \right)
\]

Now, the energy required for deformation comes from the kinetic energy of the tip impacting on the sample surface. It is the product of the force to deform one asperity and the total sliding distance and can be written as,

\[
e\frac{mV^2}{2} = \left(H\pi a_0^2\right)a_0 \text{ for plastic contacts}
\]

and

\[
e\frac{mV^2}{2} = \left(E^\ast\left(\frac{\sigma_p}{R_p}\right)^{\frac{1}{2}}\pi a_0^2\right)a_0 \text{ for elastic contacts}
\]

where, \( m = \) equivalent mass of the tip, and

\( e = \) fraction of kinetic energy due to relative sliding motion that is expended in deformation

Thus, for given contacting surfaces and a given normal load, wear will initiate only after sufficient energy is available for deformation, i.e. once sliding velocity is high enough. Below a certain critical velocity there will be no frictional losses due to deformation.

Once wear starts, we have from eq. (3.22), \( a_0 \sim V^{2/3} \). Substituting in eq. (3.21) we can write the deformation related friction force contribution as,
\[ F_{\text{def}} = \frac{\pi N_0}{z} kF_N V (1 - \exp(-\phi_{\text{def}} V^{4/3})) \]  

(3.23)

where, \( \phi_{\text{def}} = \frac{1}{8R} \left( \frac{\varepsilon m}{2\pi H} \right)^{2/3} \) for plastic contacts

and \( \phi_{\text{def}} = \frac{1}{8R} \left( \frac{\varepsilon m}{2\pi E_r \left( \frac{\sigma_p}{R_p} \right)^{1/2}} \right)^{2/3} \) for elastic contacts

(3.24)

If the normal load is small, that is, normal load itself does not cause plastic deformation, then the friction force due to deformation will become dominant only at higher sliding velocities, when the energy from impacts is higher. In such a case, there can be a clear distinction between the adhesive friction force regime and the deformation related friction force regime. Thus we can replace the \( F_N \) term in eq. (3.23) by \( W \). We can further simplify eq. (3.23) by using Taylor series expansion of the exponential term and neglecting higher order terms. Thus, the eq. (3.21) can be written as

\[ F_{\text{def}} = \mu_{\text{def}} W \]

where, \( \mu_{\text{def}} = \frac{\pi N_0}{z} \phi_{\text{def}} kV^{7/3} \)

(3.26)

The deformation related friction force increases monotonically with sliding velocity. This increase is similar to our experimental data for Si (100) sample (Fig. 3.1 (a)). It has to be noted, though, that the increase in the deformation related friction force will not continue forever as sliding velocity is increased. At very high sliding velocities there will be larger energy dissipation at the contacting asperities creating very high flash temperatures. Once the temperatures increase beyond a certain value, localized melting will set in and friction
force will again drop. The sliding mechanism at this point will become that of viscous shearing of the melted contact zone.

3.4.1.3 Atomic scale-stick slip contribution to friction force

The term stick-slip, first coined by Bowden and Leben (1939), corresponds to the build up of the friction force to a certain value, the static friction force, followed by slip at the interface once this force is overcome. The analysis of stick-slip is of particular importance in tribology because of its potential to cause damage and wear of moving parts and various models have been proposed to explain this behavior (Ruths et al., 2004). Rabinowicz (1995) uses a model for rough surfaces which produces irregular stick-slip. Bhushan (1999b) uses a spring-dashpot mechanism to model the displacement of a block as a function of time during stick-slip behavior. Berman and Israelachvili (1999) use the phase transition model to explain how thin liquid films alternately freeze and melt as they are sheared.

Stick-slip on the atomic scales is the result of the energy barrier required to be overcome for jumping over atomic corrugations on the sample surface. Stick-slip on highly oriented pyrolytic graphite (HOPG) has been reported by Mate et al. (1987) and Ruan and Bhushan (1994). Figure 3.6 shows the AFM images for surface roughness and friction force measured on a HOPG sample and 2D cross sectional profile of the friction force measured in the forward scanning direction (Ruan and Bhushan, 1994). Figure 3.7 shows how a perfect tip with only one atom at its apex would slide over the atomic corrugations on the sample surface. Atomic stick-slip during sliding can be modeled using a two spring model and it has been shown that the energy can be dissipated mainly
Figure 3.6: AFM images showing topography and friction data measured on a freshly cleaved sample of HOPG and 2D cross-sectional profile of friction force at a particular scan location revealing atomic scale stick-slip (Ruan and Bhushan, 1994)
Figure 3.7: Schematic illustrating various dominant regimes of friction force at different relative sliding velocities from atomic scale stick-slip at low velocities to deformation related energy dissipation at high velocities (Tambe and Bhushan, 2005b).
in the macroscopic degrees of freedom of the cantilever or in the microscopic degrees of freedom of the tip-sample contact (Bhushan, 1999a).

Atomic scale stick-slip has been used to explain friction on the microscales using a stress-modified thermally activated Eyring model by Bouhacina et al. (1997) and a modified Tomlinson model, taking into account the effects of thermal activation, by Gnecco et al. (2000). The stick-slip related friction force in this case is found to increase logarithmically with an increase in sliding velocity, \( V \), up to a certain critical sliding velocity, \( V_b \), and then level off. The velocity dependence is due to thermal activation of the irreversible jumps of the tip by overcoming the energy barrier between two adjacent atomic positions. Mathematically it is given as (Bouhacina et al., 1997; Gnecco et al., 2000; Riedo et al., 2003)

\[
F_{\text{stick-slip}} = c \ln\left(\frac{V}{V_b}\right)
\]  

(3.27)

where, \( c \) = characteristic constant for given tip-sample material

For dry (unlubricated) samples included in our study, the meniscus force contribution dominates (at low sliding velocities) for Si (100) and so we do not expect atomic stick slip to play a role for Si (100). In case of DLC sample, we do see the logarithmic increase as has also been reported earlier by Riedo et al. (2002).

3.4.1.4 Integrating various components of nanoscale friction

Based on the analytical theory developed so far, taking into consideration the various factors contributing to nanoscale friction, we can now integrate all the results together to yield a single mathematical expression relaying the velocity dependence of
friction force from atomic scales to micro/nanoscales for dry (unlubricated) and lubricated interfaces as well as for interfaces which are hydrophobic and hydrophilic. The total friction force is therefore,

\[
F = F_{\text{adh}} + F_{\text{def}} + F_{\text{stick-slip}}
\]

\[
= \phi_{\text{adh}} \left( W - \phi_m R \ln \left( \frac{V}{V_a} \right) \right) \left( \alpha r_a + (1 - \alpha) \frac{\eta V}{h} \right)
\]

\[
+ \frac{\pi N_0}{z} kF_n V (1 - \exp(-\phi_{\text{def}} V^{4/3})) + c \ln \left( \frac{V}{V_b} \right)
\]

In Fig. 3.7, the dominant mechanisms of friction force at different relative sliding velocities are schematically shown for a dry hydrophobic sample surface. Figure 3.8 gives the comprehensive analytical expression for nanoscale friction and its velocity dependence. Various terms indicating the dominant friction mechanisms are shown and their relative order of precedence with respect to sliding velocity is illustrated. It should be noted that this precedence order is not necessarily valid for all cases and depends on the nature of the sliding interface.

### 3.4.2 Molecular spring model for compliant SAMs

The velocity dependence of friction force for compliant SAMs cannot be explained using the analytical model given by eq. (3.28) above. In the case of HDT samples used in this study, friction is governed by the viscoelastic behavior of the SAM molecules. Liu and Bhushan (2002) have shown that there is an increase in friction force with velocity for compliant SAM molecules such as HDT and MHA (16-mercaptohexadecanoic acid thiol). They proposed a molecular spring model that explained how SAMs reorient under the tip normal load. Tambe and Bhushan (2005b)
Figure 3.8: Comprehensive analytical expression for velocity dependence of nanoscale friction with the dominant friction mechanisms (Tambe and Bhushan, 2005b)
extended the molecular spring model to explain the velocity dependence of friction for compliant SAMs. As shown in Fig. 3.9, the HDT molecules orient by tilting through a certain angle, dependent on the normal load, in the direction of motion of the tip (in the schematic in Fig. 3.9 the initial orientation of the molecules is not shown to avoid complexity). As the tip proceeds along the scan direction, the molecules are ‘relieved’ from the tip load and reorient to their initial position. Monte Carlo simulation of the mechanical relaxation of CH₃(CH₂)₁₅SH SAM performed by Siepmann and McDonald (1993) indicated that SAMs respond nearly elastically to microindentation by an AFM tip under a critical normal load. They suggested that the monolayer could be compressed, leading to a major change in the mean molecular tilt (i.e. orientation), but that the original structure is recovered as the normal load is removed. Garcia-Parajo et al (1997) observed the compression and relaxation of octadecyltrichlorosilane (OTS) film in their tests while Liu and Bhushan (2002) confirmed similar behavior on various SAMs including the HDT that we used in this study. Gourdon et al. (1997) have reported a strong dependence of molecular organization of Langmuir-Blodgett films physiosorbed on mica substrates on friction force measured during forward and reverse scans.

In the experiments, run over a range of velocities between 1 µm/s and 10 mm/s over a scan size of 25 µm, the maximum time available for reorientation for the most distant molecule on the scan path, before the tip returns at that same location while scanning, will correspondingly vary between the two extremes of 50 s and 5 ms. There will be a critical time taken by the SAM molecules to reorient and this time would be a function of the packing density, molecule complexity, and the angle through which the molecules have to spring back (Joyce et al., 1992). When more time is available for
Figure 3.9: Molecular spring model for compliant SAMs showing friction force variation with velocity during the trace and retrace scans corresponding to the molecule reorientation after relaxation of tip normal load (initial molecular tilt is not shown to avoid complexity) (Tambe and Bhushan, 2005b)
reorientation before the tip reaches the same location on the sample surface again, most of the molecules in the wake of the tip scan direction will spring back. But as velocity increases fewer molecules get sufficient time to reorient and these molecules now oppose the tip motion. Thus, at higher velocities, the friction force is higher when the tip is returning.

Assuming that the reorientation of molecules follows linearly with time, the average friction force is inversely proportional to the time available for molecular reorientation and one can then estimate friction force directly from the velocity and find that it follows a linear relation to the velocity. Figure 3.9 shows variation of friction force with time during trace and retrace scans. The average friction force over one complete cycle (trace plus retrace) can be easily determined based on the schematic in Fig. 3.9. The total friction force, $F$, over one scan cycle is the ratio of the total frictional energy dissipated in one cycle to the total sliding distance ($s$).

$$F = \frac{1}{2} \left( F_{\text{trace}} + F_{\text{retrace}} \right) \quad (3.29)$$

where, $F_{\text{trace}}$ and $F_{\text{retrace}}$ are the total friction forces during the trace and retrace scans. For a critical sliding distance $s_c$, over which the molecules do not get sufficient time for reorientation, we can determine the total friction force as

$$F = F_0 + \frac{s}{4s_c} \left( F_1 - F_0 \right), \text{ for } s \leq s_c \quad (3.30)$$

where $F_0$ and $F_1$ are the maximum and minimum values of friction forces as shown in the schematic in Fig. 3.9.

The friction force can be expressed as a function of the ratio of actual sliding velocity, $V$, to the critical sliding velocity, $V_c$, corresponding to the maximum time
required by the farthest molecule on the scan path to return to its initial orientation, and the expression for the friction force at different velocities can thus be written as below

\[
F = F_0 + \left( \frac{F_1 - F_0}{4V_c} \right) V \quad \text{for } V \leq V_c
\]

\[
F = \left( \frac{F_0 + 3F}{4} \right) \quad \text{for } V > V_c
\]

(3.31)

Once the critical velocity is reached, no molecules over the entire tip sliding distance have sufficient time to reorient and the friction force will then stabilize and reach a plateau. We therefore see a linear increase in friction force with velocity initially and for higher velocities the friction force levels off. This is similar to the data presented by Liu and Bhushan (2002). Their data at high normal loads clearly shows a linear increase in friction force followed by a distinct plateau beyond a certain critical velocity.

It should be noted that in deriving these equations it is assumed that the molecules have no initial tilt angle. Any initial tilt angle will change the friction forces measured while sliding in the direction of the molecular tilt and while sliding in a direction opposite to that. Smaller the tilt angle, larger will be the difference in the friction force measured over one scan cycle. The molecule reorientation at different velocities will however follow the same rule always and thus the molecular spring model used to derive the friction force above in eq. (3.31) remains unaffected.

### 3.4.3 Adhesion and deformation hysteresis model for polymers

Polymers form a special class of materials and owing to their viscoelastic nature friction force is largely affected by the viscoelastic recovery during sliding, deformation
and adhesion hysteresis (Moore 1972; Bhushan, 1999b). Tabor (1958) extended the concept that coefficient of friction includes both adhesion and deformation terms to polymers and demonstrated that the latter becomes significant for a high hysteresis polymer. At any given operating temperature, the increase of sliding velocity produces an adhesion peak at creep velocities and hysteresis peak at very high velocities (Moore, 1972). The adhesion component of the friction force, $F_{adh}$, for an polymer may be attributed to a molecular bonding of exposed surface atoms in both members, according to a stretch, break and relaxation cycle of events. The deformation term, $F_{def}$, is due to a delayed recovery of the polymer after indentation by a particular asperity and gives rise to what is generally called the hysteresis component of friction, $F_{hyst}$. Modern theories of adhesion in a given velocity and temperature range have described adhesion as a thermally activated molecular stick-slip process (Moore, 1972). Assuming negligible interaction between the adhesion and deformation processes and the stick-slip during sliding, we can add them (see Fig. 3.10) (Bhushan, 1999b; Moore, 1972). The total friction force, $F$, is therefore,

$$ F = F_{adh} + F_{def} = F_{adh} + F_{hyst} $$ (3.32)

Unlike a hard material, the polymer structure is composed of flexible chains which are in a constant state of thermal motion. During relative sliding between a polymer and a hard surface, the separate chains in the surface layer attempt to link with molecules in the hard base, thus forming junctions. Sliding action causes these bonds to stretch, rupture and relax before new bonds are made, so that effectively the polymer molecules jump a molecular distance to their new equilibrium position. Thus, a
Figure 3.10: Schematic illustrating multiasperity interaction at the tip-sample interface for a soft polymer sample. The principal components of friction, adhesion and deformation (hysteresis), and their cause are illustrated.
dissipative stick-slip process on a molecular level is fundamentally responsible for adhesion and several theories exist to explain this phenomenon (Moore, 1972).

On a macroscopic level, both adhesion and hysteresis can be attributed to the viscoelastic properties of the polymer. If we define a complex modulus $E^*$ as the ratio of stress to strain for a viscoelastic body, it can be shown from viscoelastic theory that:

$$E^* = E' + jE''$$  \hspace{1cm} (3.33)

where $E'$ is the storage modulus or stress-strain ratio for the component of strain in phase with the applied stress and $E''$ is the loss modulus or stress-strain ratio for the component of strain $90^\circ$ out of phase with the applied stress. The ratio of the energy dissipated (whether in the stretch and rupture cycle of individual bonds in the molecular adhesion model, or in the deformation and recovery cycle associated with hysteresis) to energy stored per cycle is defined as the tangent modulus and is given by

$$\tan \delta = \frac{E^*}{E'}$$  \hspace{1cm} (3.34)

The adhesion and hysteresis components of friction are given by (Moore, 1972)

$$F_{adh} = K_2 \frac{E'}{p'} W \tan \delta$$, and $$F_{hyst} = K_3 \left( \frac{p}{E'} \right)^n W \tan \delta$$ \hspace{0.5cm} \text{where, } n \geq 1$$  \hspace{1cm} (3.35)

where $p$ is the nominal pressure, $r$ is an exponent with a value in the neighborhood of 0.2 and $K_2$ and $K_3$ are constants dependent on the particular sliding combination.

Combining above two equations (3.34) and (3.35) we obtain,

$$F = F_{adh} + F_{hyst} = K_2 \left[ \frac{E'}{p'} + K_4 \left( \frac{p}{E'} \right)^n \right] W \tan \delta$$  \hspace{1cm} (3.36)
Thought the velocity dependence of friction force is not directly evident from equation (3.36), both the terms, $E'$ and $\tan \delta$ have to measured at the frequency of deformation and are thus velocity dependent (Bhushan, 1999b).

### 3.5 Dominant friction force regimes on the nanoscale

The analytical and molecular spring models developed to explain nanoscale friction behavior can be used to explain experimental results for various samples. The experimental data suggests two distinct regimes for all the samples studied and the reversals in friction force are seen to occur close to the 100-500 $\mu$m/s velocity range. However, each has a different friction mechanism acting at different relative sliding velocities. Table 3.3 gives the analytical expressions relating the friction force to the sliding velocity for all the samples at different velocities.

#### 3.5.1 Dry (unlubricated) hydrophilic solids

For hydrophilic interfaces meniscus forces dominate at low velocities and hence the contributions of atomic stick-slip can be neglected. Moreover the contribution of viscous shearing of the water film, at contacting and near contacting asperities where menisci are formed, to the adhesive friction force is very small and can be neglected in most instances (Bhushan, 1999b). For such a case the eq. (3.14) reduces to

$$F_{\text{adh}} \sim \mu_{\text{adh}} \left( W - \phi_m R_s \ln \left( \frac{V}{V_a} \right) \right)$$

where, $\mu_{\text{adh}} = \phi_{\text{adh}} \tau_a$
As $V$ approaches $V_a$, the meniscus contribution decreases and friction force drops, until at a critical velocity $V = V_a$, when the sliding velocity is too high for stable menisci to form anywhere at the interface and this is when the friction force levels off. At this point the adhesive friction force contribution to the overall friction force diminishes and friction is now dominated only by deformation related friction force and stick-slip. If the normal load is small, that is, normal load itself does not cause plastic deformation, then the friction force due to deformation will become dominant only at higher sliding velocities, when the energy from impacts is higher. In such a case, there can be a clear distinction between the adhesive friction force regime and the deformation related friction force regime. Thus we can replace the $F_N$ term in eq. (3.23) by $W$. We can further simplify eq. (3.23) by using Taylor series expansion of the exponential term and neglecting higher order terms. Thus, the eq. (3.21) can be written as

$$F_{\text{def}} = \mu_{\text{def}} W$$

where, $\mu_{\text{def}} = \frac{\pi N_0 \phi_{\text{def}}}{z} kV^{7/3}$ (3.38)

Thus the expression for nanoscale friction for a dry (unlubricated) solid material is

$$F = \mu_{\text{adh}} \left( W - \phi_m R \ln \left( \frac{V}{V_m} \right) \right) + \frac{\pi N_0}{z} kF_N V^{7/3}$$

(3.39)

This expression is valid for Si (100) which is an unlubricated hydrophilic solid.

For Si (100), meniscus forces dominate only at low velocities, when there is sufficient time available for stable menisci formation at the tip-sample interface. At higher velocities, Si (100) shows a non-linear increase in friction with velocity and this is attributable to the energy dissipation by asperity deformations at the tip-sample interface.

For moderately high velocities, a tribochemical reaction has been reported to occur,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Analytical expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (100) (unlubricated, hydrophilic)</td>
<td>$F = \mu_{\text{adh}} \left( W - \phi_n R \ln \left( \frac{V}{V_a} \right) \right)$</td>
</tr>
<tr>
<td></td>
<td>or $F = F_0 - F_1 \ln(V)$ (meniscus force contributions)</td>
</tr>
<tr>
<td></td>
<td>$F = \frac{\pi N_0}{z} k W V^{7/3}$</td>
</tr>
<tr>
<td></td>
<td>or $F = F_2 V^{7/3}$ (asperity impact deformations)</td>
</tr>
<tr>
<td>DLC (hydrophobic)</td>
<td>$F = \mu_{\text{adh}} W + c \ln \left( \frac{V}{V_b} \right)$</td>
</tr>
<tr>
<td></td>
<td>or $F = F_0 + F_1 \ln(V)$ (atomic stick-slip)</td>
</tr>
<tr>
<td></td>
<td>$F = \mu_{\text{adh}} W$</td>
</tr>
<tr>
<td></td>
<td>$+ \frac{\pi N_0}{z} k F_N V (1 - \exp (- \phi_{\text{def}} V^{4/3}))$</td>
</tr>
<tr>
<td></td>
<td>Phase transformation</td>
</tr>
<tr>
<td>HDT (compliant SAM)</td>
<td>$F = F_0 + \left( \frac{F_1 - F_0}{4 V_c} \right) V$ for $V \leq V_c$</td>
</tr>
<tr>
<td></td>
<td>or $F = F_0' + F_1' V$ (molecular reorientation)</td>
</tr>
<tr>
<td></td>
<td>$F = \left( \frac{F_1 + 3 F_0}{4} \right)$ for $V &gt; V_c$</td>
</tr>
<tr>
<td>HDT (compliant SAM)</td>
<td>$F = \mu_{\text{adh}} W \eta V$</td>
</tr>
<tr>
<td>Z-15 (liquid, PFPE lubricant)</td>
<td>$F = \phi_{\text{adh}} W \frac{\eta V}{h}$</td>
</tr>
<tr>
<td></td>
<td>or $F = F_2 V$ (viscous shearing of mobile lubricant film)</td>
</tr>
</tbody>
</table>

Table 3.3: Analytical expressions for friction force at different sliding velocity and the corresponding dominant friction regimes for various samples.
Table 3.3 continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analytical expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low velocity regime</strong></td>
<td><strong>High velocity regime</strong></td>
</tr>
<tr>
<td>Z-DOL (solid-like PFPE lubricant)</td>
<td>$F = \mu_{adh} W + c \ln \left( \frac{V}{V_b} \right)$ or $F = F_0 + F_1 \ln(V)$ (stick-slip)</td>
</tr>
<tr>
<td></td>
<td>$F = \frac{\pi N_0}{\frac{3}{7} \frac{2}{\pi}} k_{f_{def}} W V^{7/3}$ or $F = F_2 V^{7/3}$ (tip impacts solid-like phase dissipating frictional energy)</td>
</tr>
<tr>
<td>PMMA (polymer)</td>
<td>$F = \mu_{adh} W + c \ln \left( \frac{V}{V_b} \right)$ or $F = F_0 + F_1 \ln(V)$ (stick-slip)</td>
</tr>
<tr>
<td></td>
<td>$F = \frac{\pi N_0}{\frac{3}{7} \frac{2}{\pi}} k_{f_{def}} W V^{7/3}$ or $F = F_2 V^{7/3}$ (tip impacts solid-like phase dissipating frictional energy)</td>
</tr>
<tr>
<td>PDMS (polymer)</td>
<td>$F = A_r \tau_{o} - A_r (\tau_{o} + \alpha' \rho_r) \left( \frac{E'}{p'} + K' \left( \frac{p}{E'} \right)^n \right) \tan \delta$</td>
</tr>
</tbody>
</table>

Table 3.3: Analytical expressions for friction force at different sliding velocity and the corresponding dominant friction regimes for various samples
wherein a low shear strength layer of Si(OH)$_4$ is formed at the tip sample interface (Mizuhara and Hsu, 1992; Liu and Bhushan 2003a). This Si(OH)$_4$ layer is continuously removed and replenished, causing a drop in friction force with velocity, similar to the one resulting from the diminishing meniscus force contributions. However, formation of Si(OH)$_4$ also corresponds to an increase in the adhesive force and can thus be distinguished easily. At higher velocities deformation and wear of interface resulting from impacting asperities causes friction force to increase again. The dominant regimes of the velocity dependent friction force acting at the tip sample interface for Si (100) are schematically illustrated in Fig. 3.11.

### 3.5.2 Wet (water film or mobile lubricant) solids

For wet surface, i.e. surfaces having either a water film or mobile lubricant film the deformation component of friction force is not dominant and can be neglected. In this case at low velocities meniscus forces dominate and at high velocities viscous fluid film shearing is the dominant mechanism and the expression for nanoscale friction thus becomes

$$F = \mu_{adh} \left( W - \phi_m R_i \ln \left( \frac{V}{V_i} \right) \right) + \phi_{vis} W \frac{\eta V}{h}$$

(3.40)

This expression is valid for Z-15 which is a mobile lubricant. For Z-15, the friction force is seen to once again follow a similar trend as seen with Si (100) at low velocities. There is a logarithmic decrease in friction force with velocity initially that is attributable to diminishing meniscus force contributions to the friction force. In case of Z-15, menisci are formed by condensed water and the Z-15 molecules. As velocity
Figure 3.11: Velocity dependence of friction and adhesion with dominant friction mechanisms at different sliding velocities for Si (100), DLC, HDT, Z-DOL, Z-15, PMMA and PDMS
increases, there isn’t sufficient time available for formation of stable menisci and consequently the friction drops. At high velocities, no menisci are formed but as the tip slides over the interface there is a pure viscous film shearing effect that dictates the friction force behavior. Thus we see a linear increase in friction at high velocities. The two dominant mechanisms are schematically illustrated in Fig. 3.11.

3.5.3 Dry (unlubricated) hydrophobic solids

For hydrophobic surfaces meniscus forces are not the dominant friction mechanism and atomic stick-slip is more significant at low velocities. At high velocities, once again deformation is the dominant mechanism for solids and the expression for nanoscale friction can be reduced to the following form

$$F = c \ln \left( \frac{V}{V_b} \right) + \mu_{\text{adh}} W + \frac{\pi N_0}{z} kF_N V^{7/5}$$

(3.41)

This expression is valid for DLC which is an unlubricated hydrophobic solid. Unlike the results obtained for Si (100), experiments run on the DLC sample show an initial logarithmic increase in friction force followed by a near logarithmic decrease with velocity. The DLC film is partially hydrophobic and can absorb only a few water molecules in ambient conditions (Liu and Bhushan, 2003b). Previous researchers (Riedo et al., 2002) have shown that friction force increases logarithmically with sliding velocity for DLC. In fact we find that their predicted value for the critical velocity of 400 μm/s is very close to the velocity at which we see a reversal in friction force and a corresponding increase in the adhesive force in our experimental results. Table 3.3 gives the analytical relation for velocity dependence of friction force at low velocities. The difference
between the expression for Si (100) and DLC is that while for Si (100) the slope is negative, for DLC the slope is positive (F1 in Table 3.3).

Beyond the critical velocity, the friction force drops nearly logarithmically with any further increase in velocity. The decrease in the friction force with velocity for DLC is the result of formation of an interfacial layer of low shear strength. Friction induced phase transformation of DLC to graphite by a sp³ to sp² phase transition has been shown to occur by Voevodin et al. (1996) and Tambe and Bhushan (2005e). For DLC, in most cases, the tribological behavior appears to be controlled by a low shear strength layer formed during sliding of the surfaces in contact. Experiments with DLC have shown a decrease in the coefficient of friction with increasing load and speed; and this decrease has been attributed to an increase in the thickness of the low shear strength layer (Grill, 1997; Tambe and Bhushan, 2005e). At high velocities, the high contact pressures combined with the high frictional energy dissipation due asperity impacts at the contacting asperities on the tip-sample interface accelerate the phase transformation process.

Experiments run to study the velocity dependence of friction force for highly oriented pyrolytic graphite (HOPG) (Fig. 3.2 inset) reveal that for HOPG, friction force initially increases with velocity as a result of atomic stick-slip, but then levels off beyond a certain critical velocity. The friction force values we measured for DLC and HOPG at the highest velocity of 10 mm/s are almost the same. Moreover in our experiments for DLC we also find that the decrease in friction force is followed by an increase in adhesive force. The adhesive force increased from about 20 nN at 10 µm/s to around 45 nN at 10 mm/s. Adhesive force measurements done on HOPG using the FCP technique.
showed that HOPG has an adhesive force of 50-60 nN. We therefore believe that the decrease in friction force beyond a certain critical velocity in our experiments is the result of phase transformation of DLC that yields a low shear strength layer. Figure 3.11 schematically shows such a layer at the tip sample interface.

3.5.4 Compliant SAMs: Molecular spring model

Based on the molecular spring model developed for compliant SAMs, the friction data for HDT can be demarcated into two distinct friction force regimes, one where the friction force increases linearly with the velocity and the other where friction force is independent of the sliding velocity. Previously published data (Liu and Bhushan, 2003a) showed a logarithmic increase in friction force with velocity at low loads but at higher normal loads a linear increase followed by a constant friction force regime was distinctly seen. The adhesive force data presented here clearly shows a change in friction behavior beyond a certain critical velocity. We therefore believe that the friction force behavior can be explained by the molecular spring model even though the transition between the friction force regimes is not distinct at low normal loads. Previous studies by Clear and Nealey (2001) suggest that a viscous drag acts on the tip and plays a significant role in determining the overall friction behavior at high velocities for SAMs. The rapid increase in adhesive force beyond a critical velocity observed in our experiments must be the result of higher pull-off forces due to such a viscous drag.

Based on the experimental data in Figs 3.2 and 3.3, the analytical models developed in the previous section and with the help of the illustrations in Figs. 3.11
showing the various dominant regimes for the samples studied, the velocity dependence of friction force for all the samples can now be summarized as shown in Fig. 3.12.

Figure 3.12: Schematic illustration of tip-sample interaction at different sliding velocities depicting the various friction mechanisms and the corresponding effect on the sliding interface for Si (100), DLC, HDT, Z-DOL, Z-15, PMMA and PDMS

continued
Figure 3.12 continued

Z-DOL

Smooth sliding

AFM tip

Z-DOL

Si (100)
substrate

Solid like phase causes energy
dissipation due to impacts

Impact locations

Z-15

Meniscus contributions

Meniscus bridges

AFM tip

Z-15

Si (100)
substrate

Viscous fluid film shearing

Viscous fluid film shearing

PMMA

Smooth sliding

AFM tip

PMMA

Glass
substrate

High energy dissipation
leading to high flash temperatures

Impacts leading to localized melting

PDMS

Stick-slip dominates

Stuck contact zone

Lumpy release after slip

AFM tip

PDMS

No stick-slip
smooth sliding

Increasing velocity
3.6 Effect of rest time and acceleration (instantaneous changes in sliding velocity)

Rest time and acceleration studies are conducted to study the adhesive force dependence on rest time. It is well known in the magnetic data storage industry that the stiction (static friction) force at the head-medium interface increases rapidly with an increase in rest time (Bhushan, 1999b, 2000; Bhushan and Zhao, 1999; Liu and Bhushan, 2003a, 2003b; Bhushan et al., 2004). Stiction is also a leading cause of failure in many MEMS/NEMS applications (Maboudian and Howe, 1997; Bhushan, 1998, 2003; Tas et al., 1996) and it is important to evaluate the effect of rest time and sudden high accelerations after long periods of rest. Recently Tambe and Bhushan (2005a) have investigated the effect of rest time and acceleration at high sliding velocities.

Figure 3.13 gives the adhesive force dependence on rest time. For hydrophilic samples such as Si (100) and the mobile lubricant Z-15, the adhesive force increases with an increase in the rest time and then reaches an equilibrium value. Such behavior has been reported before (Bhushan, 2003; Liu and Bhushan, 2003a, 2003b; Tambe and Bhushan, 2005a) and is the result of formation of meniscus bridges at the contacting interface. Further the increase in adhesive force with rest time has been shown to be logarithmic in nature (Bouquet et al., 1998; Chilamakuri and Bhushan, 1999; Tambe and Bhushan, 2005b).

In the presence of a thin liquid film such as lubricant or adsorbed water layer at the tip-sample interface, menisci bridges form around the contacting and near contacting asperities due to surface energy effects. The attractive meniscus force arises from the negative Laplace pressure inside the curved menisci and is given by the product of this pressure difference and the immersed surface area of the asperity (Bhushan, 1999b). The
Figure 3.13: Rest time dependence of adhesive force for various materials, coatings and lubricants measured using Si₃N₄ tips at a sliding velocity of 4 µm/s at 20 °C and 50 % RH.
total meniscus force, $F_m$, at the sliding interface is obtained by summing up the meniscus forces at all the individual contacting and non-contacting asperities where menisci are formed (Bhushan, 1999b; Tambe and Bhushan, 2005b) and is given by the expression

$$F_m = 2\pi R_t \gamma (\cos(\theta_1) + \cos(\theta_2)) N(t)$$

where, $R_t =$ radius of the contacting tip

$\gamma =$ surface tension of the liquid film

$\theta_1$ and $\theta_2 =$ contact angles for the sample and the tip

$N(t) =$ number of contacting and near contacting asperities where menisci build up

The number of menisci bridges is a function of time. As rest time increases more menisci bridges build up at the contacting and near-contacting asperities (Bocquet et al., 1998; Bhushan, 2003; Tambe and Bhushan, 2005b). Figure 3.14 schematically illustrates the build-up of meniscus bridges with increasing rest time.

Unless the surface is covered with a liquid film, the surface hydrophobicity dictates the meniscus bridge formation at the interface. Contact angle is a direct measure of the surface hydrophobicity and depending upon whether the contact angle is <90° or >90° the surface is termed as hydrophilic or hydrophobic. Table 3.4 gives the water contact angles for various samples. Except Si (100) and Z-15 the rest of the samples are either partially or completely hydrophobic and hence show negligible or no rest time dependence.

Figure 3.15 shows the effect of acceleration (change in instantaneous sliding velocity) on the friction force and adhesive force. It was found that as acceleration increased, the slopes of the friction force vs. velocity and adhesive force vs. velocity curves decreased. This implies that for the same rest time, higher accelerations result in a
Figure 3.14: Schematic showing the effect of increasing rest time on adhesive force due to build up of meniscus bridges between the contacting and near contacting asperities at the tip-sample interface (Tambe and Bhushan, 2005a)
Table 3.4: Brief description of sample preparation

<table>
<thead>
<tr>
<th>Material</th>
<th>Contact angle (Tambe and Bhushan 2004b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (100)</td>
<td>35</td>
</tr>
<tr>
<td>DLC</td>
<td>60</td>
</tr>
<tr>
<td>PMMA</td>
<td>74</td>
</tr>
<tr>
<td>PDMS</td>
<td>105</td>
</tr>
<tr>
<td>HDT</td>
<td>97</td>
</tr>
<tr>
<td>Z-15</td>
<td>48</td>
</tr>
<tr>
<td>Z-DOL</td>
<td>72</td>
</tr>
</tbody>
</table>

Figure: 3.15: Effect of rest time and instantaneous velocity (change in acceleration) for Si (100) with native SiO₂

Figure: 3.15: Effect of rest time and acceleration (change in instantaneous velocity) on the friction and adhesive forces for Si (100) (Tambe and Bhushan, 2005a)
higher adhesive force. We can model the rest time effect taking into consideration the contribution of the meniscus force to the overall adhesive force. However, apart from the meniscus force, $F_m$, the viscous force, $F_v$, required for shearing the fluid film when initiating motion can also play a role in determining the total adhesive force, $F_{adh}$, encountered by the tip at the tip-sample interface (Bhushan, 1999b) and is given by the following relation

$$F_{adh} = F_m + F_{v\perp}$$  \hspace{1cm} (3.42)

In this expression, $F_{v\perp}$ corresponds to the component acting perpendicular to the sliding direction. It should be noted that the component of the adhesive force arising from adhesion between the tip and sample is neglected in this expression since it is independent of the rest time and the acceleration.

For hydrophilic samples, the meniscus force decreases logarithmically with velocity and this velocity dependence can be given by the eq. (3.12) developed in the above section

$$F_m = -c_1 \ln(V)$$  \hspace{1cm} (3.43)

where $c_1$ = constant depending on the material of the two surfaces in contact and the interface conditions (such as relative humidity)

The viscous component is significant mostly for viscous liquids (dynamic viscosity ~1 Pa s) but can dominate even for liquids of modest viscosities at high shear rates (Bhushan, 1999b). The time required to separate the two surfaces is inversely proportional to the velocity (and acceleration) and therefore, for higher accelerations, the viscous component of the adhesive force becomes more significant. The expression for the viscous force as a function of sliding velocity is given by Matthewson (1988) as
\[ F_{v \perp} = \sqrt{2k_sV_{i_v}} = c_2 \sqrt{V} \]  

(3.44)

where, \( k_s \) = stiffness of the loading member

\( I_v \) = critical viscous impulse that must be exceeded to overcome the viscous force,

and, \( c_2 = \sqrt{2k_sI_v} \)

Substituting the eqs. (3.43) and (3.44) in eq. (3.42), the total adhesive force is

\[ F_{adh} = F_m + F_{v \perp} = -c_1 \ln(V) + c_2 \sqrt{V} \]  

(3.45)

Figure 3.16 schematically illustrates the variation of the adhesive force components as a function of velocity. \( W \), the applied normal load, is velocity independent. Meniscus force, \( F_m \), decreases logarithmically with velocity and viscous force, \( F_{v \perp} \), increases as the square root of the velocity. At a particular velocity the meniscus force loses its dominance and viscous force contributions become more significant. Hence, for higher scan velocities, rest time does not play a big role and the viscous forces are high enough to dwarf the meniscus force contribution to the overall friction and adhesion.

Figure 3.17 shows the change in adhesive force with sliding velocity for all samples. It should be noted that for partially hydrophobic and completely hydrophobic samples the adhesive force dependence cannot be essentially explained using the meniscus force and viscous force contributions. Tambe and Bhushan (2005b) have explained the adhesive force dependence for a variety of samples. For DLC, the increase in adhesive force is believed to be the result of phase transformation of the DLC film to a grahite-like phase. For HDT, the increase in adhesive force arises from the viscous drag experienced by the tip at high velocity and the corresponding removal of SAM from the
Figure 3.16: Normal load components and their dependence on velocity. Viscous contributions increase with velocity (higher accelerations) and dominate the meniscus contributions resulting in higher adhesive and friction force (Tambe and Bhushan, 2005a)
Figure 3.17: Velocity dependence of adhesive force (effect of acceleration or the change in instantaneous velocity) for various materials, coatings and lubricants measured using Si$_3$N$_4$ tips at a normal load of 70 nN at 20 °C and 50 % RH
substrate and attachment to the scanning tip. For polymers, the velocity dependence of adhesive force is well known and many studies exist on the macro as well as microscale (Moore, 1972).

3.7 Closure

The new direct approach for friction measurement, discussed in chapter 2, developed by Tambe and Bhushan (2005a) by modifying the commercial AFM setup was employed to study the velocity dependence of nanoscale friction. Friction and adhesive force dependence on sliding velocity was studied for various materials, coatings and lubricants with hydrophobic as well as hydrophilic surface properties. The friction force and adhesive force were found to exhibit a strong velocity dependence for all samples and friction behavior showed reversals beyond certain critical velocities for all samples.

A comprehensive analytical friction model was proposed to explain friction behavior on the nanoscale over a wide range of velocities. The model is based on three major contributing factors to nanoscale friction, viz. adhesion at the tip sample interface, high impact velocity related deformation at the contacting asperities and atomic scale stick-slip. Friction behavior for the samples studied was completely explained using this analytical model and the dominant regimes for friction force at different relative sliding velocities were identified. The effect of rest time and acceleration was also investigated. Rest time behavior was found to be more significant for hydrophilic interfaces whereas acceleration effect was found to be more dependent on the specific nature of the interface and the material properties. These results are of considerable importance owing to the wide applicability of these samples in MEMS/NEMS components.
In the next chapter the effect of continuous sliding on friction, adhesion and wear at high sliding velocities is discussed. The initiation of wear and the mechanisms involved are studied.
CHAPTER 4
WEAR STUDIES: WEAR INITIATION INVESTIGATIONS, WEAR MAPPING TECHNIQUE AND WEAR MECHANISMS

4.1 Nanotechnology applications: Wear issues

Despite the increasing popularity and technological advances in MEMS/NEMS applications the severe tribological (friction and wear) problems tend to undermine their performance and reliability. The components used in micro/nanostructures are very light (on the order of few micrograms) and operate under very light loads (on the order of few micrograms to a few milligrams). Going from macro to micro/nanoscale the surface to volume ratio increases considerably and becomes a cause of serious concern from tribological point of view. On micro/nanoscale surface forces such as friction, adhesion, meniscus forces, viscous drag and surface tension that are proportional to area, significantly increase and limit the life and reliability of MEMS/NEMS devices (Komvopoulos, 2003; Maboudian and Howe, 1997; Bhushan, 1998, 2003, 2004). As a result, friction and wear of lightly loaded micro/nanostructures are highly dependent on the surface interactions. Failures in micro/nanostructures, resulting from continuous operation, are well known (Muhlstein and Brown, 1997; Arney, 2001; de Boer and Mayer, 2001; Man, 2001; Bhushan, 2004).
Many MEMS/NEMS devices are designed to operate at very high sliding velocities with rotational speeds between the mating components ranging well above 100,000 rpm in case of micromotors (Bhushan, 2004) and well above 1 million rpm in some applications such as microgas turbines (Frechette et al., 2005). Given the size of these devices (the micromotor has a rotor diameter of 120µm) the relative sliding velocities that they operate at can reach several m/s. Wear is a known issue for failure of micro/nanoscale devices and components (Tanner et al., 2000) and can result from high frictional energy dissipation due to the impacts of contacting asperities (Tambe and Bhushan, 2005b). Wear also arises from operation over a period of time as a result of fatigue. Commercial applications such as the DMD are designed for a lifetime operation of over 100,000 hr without loss in image quality. Such stringent operating conditions means the rotating micromirrors in the DMD can be subject to well over 2.5 trillion cycles during their lifetime. Fatigue induced damage of the micromirror–hinge assembly is a potential failure mechanism for DMDs (Liu and Bhushan, 2004). Wear of sliding surfaces can occur by one or more wear mechanisms, including adhesive, abrasive, fatigue, impact, corrosive and fretting and can seriously undermine reliability of these devices (Figure 4.1 shows wear of a microgear set component). Wear during contacts between spring tips and the landing sites, hinge fatigue, shock and vibration related failures are some of the important issues known to affect the reliable operation of the DMD (Liu and Bhushan, 2004).

Recent efforts, discussed in chapter 2, that are based on an alternative approach of utilizing a large amplitude relatively low resonant frequency piezo stage have allowed studies at high sliding velocities (up to 10 mm/s) (Tambe and Bhushan, 2005a) and
helped develop a fundamental understanding of friction, adhesion and wear behavior at high sliding velocities (Tambe and Bhushan, 2004b, 2005b-i). These studies would be crucial in understanding friction and wear mechanisms for most real world devices and will aid in the characterization of materials, coatings and lubricants that are considered potential solutions for various nanotechnology applications, thereby aiding the future design and development of micro/nanostructures for various nanotechnology applications.

Figure 4.1: SEM images showing a microgear set and wear of different components such as hub, clip and pin-hole from high sliding velocity (www.sandia.gov)
4.2 Experimental methodology for wear studies

4.2.1 Effect of continuous sliding on friction

Wear initiation was studied by continuously scanning on the same sample location and monitoring the change in friction force with sliding distance. Experiments were performed using square pyramidal Si$_3$N$_4$ tips and triangular pyramidal tips of single crystal natural diamond. The Si$_3$N$_4$ tips had a nominal radius of 30-50 nm and were mounted on gold coated triangular Si$_3$N$_4$ cantilevers with a nominal spring stiffness of 0.58 N/m. Experiments with Si$_3$N$_4$ tips were performed at normal loads of 70 nN and 150 nN and for sliding velocities between 1 µm/s and 10 mm/s. The diamond tip, ground to the shape of a three sided pyramid with apex angle of 80° and tip radius of about 50 nm, was bonded using an epoxy to a gold-coated stainless steel cantilever beam (20 µm thick, 0.2 mm wide and approximately 2 mm long). The stiffness of the beam was 10 N/m and was calculated using the analysis for an end-loaded cantilever beam with rectangular cross-section as described in Bhushan (1999a).

4.2.2 Nanowear mapping technique

For the nanowear mapping experiments, Si tips (coated with Ti/Pt) with nominal cantilever stiffness of 3.5 N/m and nominal tip radii of 40 nm were used. For generating nanoscale wear maps, the sample was oscillated using the piezo stage and simultaneously the AFM tip was dragged perpendicular to the direction of motion of the sample (see schematic in Fig. 4.2). The sample oscillation frequency (scan speed), the AFM tip velocity and the normal load were controlled to achieve appropriate relative sliding velocities, normal loads and a specific number of sliding cycles. The relative sliding
velocity was varied by changing the scan speed while the number of sliding cycles was varied by varying the rate of movement of the AFM tip (i.e. the velocity of the AFM tip while sliding perpendicular to the direction of motion of the sample. This varying rate of movement results in the AFM tip residing for different time intervals on the sample surface and thereby the number of sliding cycles obtained at each location on the sample surface is different.)

Figure 4.2: Novel technique for wear mapping, achieved by controlled movement of the AFM tip while the sample is sliding perpendicular to the direction of the AFM tip movement (Tambe and Bhushan, 2005e)
For all wear mapping experiments a scan size (i.e. the magnitude of sample oscillation) of 5 μm was chosen. After the wear tests the sample surface was imaged using the same AFM tip but at relatively lower normal loads. Wear maps were first obtained by varying only one parameter out of the three: normal load, sliding velocity and number of sliding cycles, at a time. For studying the effect of increasing normal load and increasing number of sliding cycles at constant sliding velocity, the AFM tip was programmed to make controlled movements at desired normal loads and velocities. This controlled motion of the AFM tip was achieved using custom software code written in NanoScript™ (Anonymous, 1999). Next wear maps were generated to study the effect of normal load and sliding velocity simultaneously. To achieve varying sliding velocities across the scan area, the input voltage pulse for the piezo stage was slightly modified. In normal operation a triangular voltage pulse is provided to the piezo stage to achieve scanning operation and to obtain a constant sliding velocity. For the wear mapping experiments, a parabolic voltage pulse was used as input to drive the piezo. This resulted in a steady increase in sliding velocity across the scan area. The synchronized and controlled movement of the AFM tip and the sample is a novel approach for obtaining nanoscale wear maps and helps generate a visual representation of the sample surface wear as a function of sliding velocity, applied normal load and number of sliding cycles (Tambe and Bhushan, 2005h). Using this approach a wear map can be generated in one single experiment, as against the rather cumbersome approach where researchers conduct multiple experiments at different normal loads, sliding velocities and for different number of sliding cycles and then generate a contour map for the sample wear based on individual data points obtained from each experiment.
4.2.3 Wear studies of SAMs

Failure of SAMs resulting from wear was studied by monitoring the decrease in surface height with an increase in normal load. Wear tests were conducted using a Si tip with nominal radius of 10 nm and nominal cantilever stiffness of 40 N/m on a 1µm × 1µm scan area at the desired normal load. A scan rate of 1 Hz was used. After each wear test, a 3 µm × 3 µm area was imaged and the average wear depth was calculated. It should be noted that wear depths stated for various SAMs corresponds to the change in the average height inside and outside of the ‘wear mark’ as discussed in the results section.

Wear studies were conducted on various kinds of SAMs having different chemical structures, backbone chains, head and tail groups, chain lengths and prepared with different deposition techniques. Two types of substrates, Al and Si (100) with a native oxide layer, were used for the SAM deposition. Various kinds of precursors with different backbone chain lengths and chain structures (hydrocarbon and fluorocarbon) as well as different deposition techniques were employed for depositing SAMs on the Al and Si substrates. The coatings deposited on Al substrates were alkyl chain phosphonic acid precursors with 8 and 18 carbon atoms, CH₃-(CH₂)ₙ-PO₂-OH (n=7 or 17), octylphosphonate (OP) and octadecylphosphonate (ODP). The coatings deposited on Si substrates were fluorocarbon precursors. The fluorocarbon precursor molecules used for deposition were Fluorinert™ (SJ040715C, FC722, solute and FC72, solvent, 3M Seoul, South Korea) and pentafluorophenyltrithoxysilane (PFPTES, 97%, No. SIP6716.7, ABCR GmbH & Co. KG, Karlsruhe, Germany). More details regarding SAMs used in this study and their preparation techniques can be found in Kasai et al. (2005), Lee et al. (2005) and Tambe and Bhushan (2005g).
4.3 **Wear studies**

In the previous section the effect of operating parameters on friction and adhesion was presented. Nanoscale friction force is seen to strongly depend on the sliding velocity for various materials, coatings and lubricants. At high sliding velocities, friction behavior is found to be governed by asperity impacts and the resulting deformations of the contacting asperities due to high frictional energy dissipation. Next we present the effect of continuous sliding on friction force to understand the wear initiation process and then investigate the wear mechanisms involved for the specific tip/sample interface.

### 4.3.1 Effect of sliding velocity on friction and wear initiation

At high velocities, higher energy dissipation due to asperity impacts is expected to have an influence on wear initiation. Tambe and Bhushan (2005c) investigated the effect of high velocity on the wear initiation for Si (100) and DLC by monitoring friction force as a function of sliding distance at two different velocities. For Si (100), experiments were performed at 10 µm/s and 10 mm/s (friction was high for both these velocities (see Fig. 4.3)). The friction force increased drastically during high velocity tests (10 mm/s) whereas it slightly decreased and leveled off at a value lower than that at the start during the low velocity tests (10 µm/s). Similar behavior was observed at normal loads of 70 and 150 nN, however, as expected, the increase in friction force was higher at 150 nN. The drastic increase is believed to be the result of a combination of factors: deformation resulting from impacts of the contacting asperities and the corresponding three-body wear due to debris particles generated at the sliding interface, and a tribochemical reaction which is accelerated by high velocities (Mizuhara and Hsu, 1992). Previous researchers
Figure 4.3: Effect of sliding velocity on durability of Si (100) and DLC measured at 70 nN and 150 nN normal load using Si$_3$N$_4$ tips at 20 °C and 50 % RH (Tambe and Bhushan, 2005c)
(Muhlstein et al., 2001) have proposed a mechanism of failure of silicon based microfilms due to high stress cycles and subsequent wear through a process of sequential mechanically induced oxidation and environmentally assisted cracking of the surface layers.

For DLC the experiments were conducted at 250 $\mu$m/s and 10 mm/s. The friction force remained fairly constant with sliding distance for the test at 250 $\mu$m/s, however, it decreased with sliding distance for the test at 10 mm/s. These results are consistent with those reported before for macroscale pin-on-disk experiments (Grill, 1997). The ultra-low wear rates and the reduction in the friction force in long duration tests have been attributed to the formation of a low shear strength layer at the sliding interface. Repeated friction is believed to accelerate the sp$^3$ to sp$^2$ phase transition of some DLC into a graphite-like phase (Voevodin et al., 1996; Grill, 1997; Tambe and Bhushan, 2005e).

The effect of continuous sliding on the tip wear was studied by estimating the tip radii before and after the tests using tip characterization software (Anonymous, 2004). In all cases the tip radius was found to have increased from the initial nominal value of 30-50 nm to around 60-75 nm. However, no specific trend was found that could suggest larger tip wear for high velocity as compared to high normal load.

### 4.3.2 Effect of continuous sliding on friction at high sliding velocities

The strong dependence of sliding velocity on the wear initiation process motivates a comparative study for all the samples. Figures 4.4 and 4.5 show the results for tests run using Si$_3$N$_4$ and diamond tips at sliding velocities of 10 mm/s and normal loads of 150 nN and 1 $\mu$N respectively. For wear studies on Si (100) and DLC, it has been shown that
higher normal loads (>10 \(\mu\)N) can lead to high tip wear (Sundararajan and Bhushan, 2001) while in case of HDT high normal loads (>5 \(\mu\)N) can wear off the HDT films from the substrate (Liu and Bhushan, 2002b).

Si (100) had the lowest durability, i.e. wear initiates the earliest amongst all samples and the friction force increased drastically after only a short sliding distance due to high deformation and wear of the contacting asperities from impacts. For Z-15, the friction force was constant initially but then increased drastically and reached a value close to that for Si (100). A similar behavior has been reported before (Koinkar and Bhushan, 1996) and the reason for this is believed to be the removal of the mobile Z-15 molecules from under the scanning tip at the sliding interface. The depletion of lubricant molecules exposes the Si (100) substrate and results in higher friction.

For DLC, phase transformation is believed to occur due to high contact pressures at the sliding interface as noted in the previous section. However, the results show that while the friction force decreased with sliding distance at low normal load with Si\(_3\)N\(_4\) tip, it increased at higher normal load with diamond tip. Diamond tip is much harder than Si\(_3\)N\(_4\) and the contact pressures are much higher for diamond tip (see Table 4.1). The increase in friction force thus suggests that the graphite-like debris particles get ejected from the interface during sliding instead of forming a thin film at the interface (Tambe and Bhushan, 2005c).

For HDT, the friction force almost remained constant over a large sliding distance. A slight drop in friction was seen towards the end of the test at low normal load and this was probably due to orientation and relocation of the SAM molecules due to continuous scanning. Liu and Bhushan (2002a) have reported that friction force can
Figure 4.4: Friction force as a function of sliding distance measured using Si$_3$N$_4$ tips at a normal load of 150 nN and a sliding velocity of 10 mm/s at 20 °C and 50 % RH (Tambe and Bhushan, 2005c)
Figure 4.5: Friction force as a function of sliding distance measured using diamond tips at a normal load of 1 µN and a sliding velocity of 10 mm/s at 20 °C and 50 % RH (Tambe and Bhushan, 2005c)
<table>
<thead>
<tr>
<th>Tip used</th>
<th>Si$_3$N$_4$</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal tip radius (nm)</td>
<td>30-50</td>
<td>50</td>
</tr>
<tr>
<td>Normal load range</td>
<td>10-150 nN</td>
<td>0.5-10 µN</td>
</tr>
<tr>
<td><strong>Si (100)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact radius (nm)</td>
<td>1.6-3.9</td>
<td>5.3-14.4</td>
</tr>
<tr>
<td>Contact pressure (GPa)</td>
<td>1.24-3.14</td>
<td>5.67-15.4</td>
</tr>
<tr>
<td><strong>DLC</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contact radius (nm)</td>
<td>1.3-3.3</td>
<td>4.3-11.7</td>
</tr>
<tr>
<td>Contact pressure (GPa)</td>
<td>1.8-4.4</td>
<td>8.6-23.3</td>
</tr>
</tbody>
</table>

Table 4.1: Contact radius and contact pressures for Si (100) and DLC samples used in the experiments. (Calculations are based on single asperity Hertzian contact analysis).
significantly reduce after several scans for compliant SAMs. At high normal load, however, a slight increase was seen in the friction force. Liu and Bhushan (2002b) have shown that SAM molecules do not wear for loads smaller than 5 µN. In the experiments, the combination of high velocity and high normal load is believed to result in the detachment and removal of some SAM molecules from the interface. This eventually exposes the underlying Au (111) substrate that has a higher coefficient of friction (Bhushan and Liu, 2001) and is the reason for increase in friction. For Z-DOL, the friction force dropped after large sliding distances for both normal loads, and similar to HDT this drop was most probably the result of some of the bonded Z-DOL molecules breaking up from the substrate and acting as a mobile lubricant fraction. Our results therefore indicate that higher sliding velocities can have a similar effect on the wear initiation process as do higher normal loads.

At low normal load, PMMA showed a constant friction force up to a certain sliding distance followed by a drastic increase. PMMA is a soft polymer (see Table 4.2) with a low melting point in the range of 85-100 °C (Becker and Locascio, 2002). The continuous sliding and the high energy dissipation from asperity impacts will subsequently lead to localized melting at the contact zone. That in turn will result in an increase the friction force. At higher normal loads, friction is higher for PMMA due to larger energy dissipation. PDMS, on the other hand, is softer than PMMA (see Table 4.2) and hence can absorb impacts even at high velocities. Consequently friction force remains fairly constant for PDMS over the entire test duration. Some localized melting may still take place due to the continuous sliding and result in an increase in friction force towards the end of the test.
<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus, $E$ (GPa)</th>
<th>Hardness, $H$ (GPa)</th>
<th>Poisson’s ratio, $\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Si}_3\text{N}_4$ tip</td>
<td>$310^{a}$</td>
<td>$20^{a}$</td>
<td>$0.22^{a}$</td>
</tr>
<tr>
<td>Diamond tip</td>
<td>$1140^{b}$</td>
<td>$80\text{-}104^{a,b}$</td>
<td>$0.07^{b}$</td>
</tr>
<tr>
<td>Si (100)</td>
<td>$130^{c,d}$</td>
<td>$11^{e}$</td>
<td>$0.28^{d}$</td>
</tr>
<tr>
<td>DLC</td>
<td>$280^{e}$</td>
<td>$24^{e}$</td>
<td>$0.25^{e}$</td>
</tr>
<tr>
<td>PMMA</td>
<td>$7.7^{f}$</td>
<td>$0.43^{f}$</td>
<td>$0.35\text{-}0.4^{g}$</td>
</tr>
<tr>
<td>PDMS</td>
<td>$360\text{-}870$ kPa$^{g}$</td>
<td></td>
<td>$0.5^{g}$</td>
</tr>
</tbody>
</table>

$^{a}$ Bhushan and Gupta (1997)
$^{b}$ Field (1992)
$^{c}$ Bhushan and Venkatesan (1993)
$^{d}$ Anonymous (1988)
$^{e}$ Bhushan (1999c)
$^{f}$ Wei (2004)
$^{g}$ Livermore and Voldman (2004)

Table 4.2: Material properties
Adhesive force was measured before and after the wear initiation studies with Si$_3$N$_4$ tips to get a measure of the change in surface properties of the sample and/or tip. The adhesive force was seen to increase for all the samples studied (Fig. 4.6). For Si (100) the increase is the result of formation of wear debris particles (Tambe and Bhushan, 2005c, h) and a tribochemical reaction that occurs at the interface (Mizuhara and Hsu, 1992) along with tip wear as noted in the previous section. DLC, on the other hand, is partially hydrophobic and tip wear does not cause the high adhesive force. The reason for high adhesive force, as stated before, is believed to be the formation of a graphite-like phase at the sliding interface (Tambe and Bhushan, 2005e). To confirm this, adhesive force measurements were performed on highly oriented pyrolytic graphite (HOPG) in ambient environment of 20 °C and 50% RH and a value of 50-60 nN was obtained (Tambe and Bhushan, 2005b, e). As the adhesive force for DLC after the test was in this range, the increase is believed to be due to phase transformation. The increase in adhesive force for HDT, Z-15 and Z-DOL is believed to be the result of some of the unbonded or displaced molecules getting attached to the tip (Tambe and Bhushan, 2005c). For PMMA and PDMS, continuous sliding leads to localized melting at the contacting asperities. This results in softening of the contact zone and is the reason for the increase in the adhesive force. The increase, however, is only marginal in case of PDMS.

Figure 4.7 summarizes the results of the wear initiation studies for various materials, coatings and lubricants at high sliding velocities. The transformations of the contact zone at the tip/sample interface are schematically illustrated.
Figure 4.6: Adhesive force values measured before and after the durability tests done using Si$_3$N$_4$ tips at a normal load of 150 nN and a sliding velocity of 10 mm/s at 20 °C and 50 % RH (Tambe and Bhushan, 2005c)
Figure 4.7: Schematic illustrating the wear mechanisms responsible for different materials, coatings and lubricants (Tambe and Bhushan, 2005c)
4.3.3 Mapping wear on the nanoscale

For wear studies, previously an AFM based ‘continuous microscratch’ technique has been developed by Sundararajan and Bhushan (2001b). That technique gave a direct dependence of the scratch depth on the applied normal load, thereby giving the critical normal load for failure for materials and coatings. This technique has been used by Liu and Bhushan (2002b) for studying wear behavior of various SAMs lubricants as well as substrates. The microscratch technique, however, doesn’t provide a dependence of normal load, sliding velocity and the number of sliding cycles simultaneously that is needed to generate wear maps. Wear maps give a direct representation of various operating conditions and can help identify and demarcate the corresponding wear mechanisms. On the macroscale, various researchers have used an approach where they run a multitude of experiments and then plot wear maps based on the failure data and rate of removal of material during wear (Bowden and Tabor, 1950, 1964; Singer and Pollock, 1992; Bhushan, 1999b). Lim and Ashby (1987) and Lim et al. (1987) constructed wear maps using empirical data as well as theoretical analysis. They demonstrated the utility of the wear-mechanism mapping method as a way of classifying and ordering wear data and of showing the relationships between competing wear mechanisms. A novel AFM based technique was developed by Tambe and Bhushan (2005h) to generate wear maps on the nanoscale by varying the sliding velocity, number of sliding cycles and the normal load.

4.3.3.1 Wear of Si (100)

Figure 4.8 gives the wear maps obtained for Si (100) by varying different operating parameters. The wear mark is roughly located in the center of each image. The arrow
marks on the sides of the AFM images indicate the beginning and end of the wear marks. A larger area was imaged after the wear mapping tests to enable comparison of worn surface with respect to the virgin surface in its vicinity. The AFM images reveal the dependence of wear on the operating parameters. Drastic failure was observed for high normal loads. This is evident from the large amount of debris found for the experiment conducted by keeping the sliding velocity and the number of sliding cycles constant at 2.5 mm/s and 500 respectively and varying normal load from 0-5000 nN. For low loads, no visible wear debris is found. Wear edges start becoming visible approximately for loads over 2000 nN and ultimately catastrophic failure is seen at and above about 4000 nN. A similar experiment was conducted by maintaining a constant sliding velocity and number of sliding cycles and varying the normal load, but the number of cycles was increased to 2500 and the normal load was varied from 0-1000 nN. In this case no catastrophic failure was observed. The wear mark was visible in the form of piled up debris at the edges. The pile-up was higher at higher normal loads. This indicates that for the given set of test parameters selected, the effect of normal load is more pronounced.

The third AFM image in Figure 4.8 corresponds to the wear map obtained by keeping the sliding velocity and the normal load constant at 2.5 mm/s and 1000 nN respectively and varying the number of sliding cycles from 0-250 across the scan area. In this case the amount of debris pile-up was minimal and the wear mark edges were barely visible.

From the velocity dependence and durability experiments, larger wear is expected at high sliding velocities and for long durations of sliding. The wear maps corroborate these findings. In most cases the high sliding velocity alone was not able to result in
Figure 4.8: Wear maps showing effect of normal load and sliding velocity, as well as effect of number of sliding cycles for Si (100) (Tambe and Bhushan, 2005h)
visible wear. Increasing the normal load accelerated the wear process and hence larger wear was found with significant debris accumulation. The increase in wear debris accumulation was however not a linear process and large amount of debris was suddenly found beyond certain normal loads.

4.3.3.2 Wear of DLC

Figure 4.9 gives the results obtained for DLC. Wear maps were obtained by varying the normal load from 0-1000 nN and keeping the number of sliding cycles and the sliding velocity constant. For experiments conducted at 200 \( \mu \)m/s, the wear mark edges were barely visible. However considerable wear was visible for a sliding velocity of 2.5 mm/s. The wear mark generated suggests that the effect of sliding velocity is more profound than that of the normal load. The larger concentration of debris particles towards the end of the wear region indicates that in general higher wear occurs for higher normal loads as expected. The effect of number of sliding cycles on wear behavior was investigated by keeping normal load constant at 500 nN and sliding velocity constant at 2.5 mm/s. The wear mark generated from these experiment shows larger accumulation of wear debris for larger number of sliding cycles. The wear marks for DLC appear “fuzzy” as the loose debris easily moves during imaging.

In comparison to Si (100), DLC sample shows larger amount of wear debris for lower normal loads and number of sliding cycles. Also the effect of sliding velocity is found to be more profound on generation of wear particles. The mechanisms of wear in both, Si (100) and DLC, are completely different. While Si (100) is a brittle material and
Figure 4.9: Wear maps showing effect of normal load and sliding velocity, as well as effect of number of sliding cycles for DLC (Tambe and Bhushan, 2005e)
wear occurs by two- and three-body abrasion, for DLC wear is the result of phase transformation as discussed in the previous sections and the debris generated is soft graphite like phase.

4.3.3.3 Nanowear mapping

The wear maps in Figs. 4.8 and 4.9 indicate that wear debris particles are generated only for certain combinations of sliding velocities, normal loads and number of sliding cycles. In these wear maps only one operating parameter was varied at a time. To obtain true wear maps that can allow investigating different wear mechanisms simultaneously, it is necessary to vary both normal load and sliding velocity and investigate the resulting wear. Here we present a nanowear map for DLC sample that was obtained by simultaneously varying the normal load and the sliding velocity over the entire scan area to investigate wear resulting from phase transformation of DLC. The wear map generated for a normal load range of 0-1000 nN and sliding velocity range of 0-2.5 mm/s in this fashion is shown in Fig. 4.10. Wear debris was seen to form only for particular sliding velocities and normal loads, i.e. beyond certain threshold frictional energy dissipation. Hence the wear area was curved indicating that for lower velocities and lower normal loads there is no phase transformation. For clarity, the wear mark corners are indicated by white dots in the AFM image and the various zones of interest over the entire wear mark are schematically illustrated in Fig. 4.10.

Analogous to nanowear mapping, nanoscale friction maps can also be generated using the same technique by monitoring the friction force during scanning. Friction force can be plotted as a function of the operating parameters: sliding velocity, normal load and
Figure 4.10: Nanowear map (AFM image and schematic) illustrating the influence of sliding velocity and normal load on the wear of DLC resulting from phase transformation. Curved area shows debris lining and is indicative of the minimum frictional energy needed for phase transformation (Tambe and Bhushan, 2005h)
the number of sliding cycles. The nanofriction mapping in conjunction with the nanowear mapping can provide valuable information regarding the operating parameter dependence of nanoscale friction and wear. Tambe and Bhushan (2005d) have demonstrated the effectiveness and utility of these techniques when used in tandem while studying the phase transformation related reduction in friction and wear of DLC.

4.3.3.4 Wear of SAMs lubricants

(Tambe and Bhushan, 2005g) investigated nanotribological properties of SAMs having different chemical structures, backbone chains, head and tail groups, chain lengths and that were prepared by different deposition techniques on two different substrates. Table 4.3 lists the SAMs studied along with the film thicknesses. Wear of SAMs was studied by monitoring the decrease in surface height with an increase in normal load. Studies by Liu and Bhushan (2003a) and Kasai et al. (2005) indicate that SAMs reorient up to a certain critical normal load but once that load is exceeded the SAMs coatings fail by shearing of molecular bonds at the SAM-substrate interface.

<table>
<thead>
<tr>
<th>SAM/substrate</th>
<th>Acronym</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octylphosphonate/Al</td>
<td>OP/Al</td>
<td>~1.9&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Octadecylphosphonate/Al</td>
<td>ODP/Al</td>
<td>~2.1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pentafluorophenyltriethoxysilane/Si</td>
<td>PFPTES/Si</td>
<td>2.2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fluorinert/Si</td>
<td>Fluorinert/Si</td>
<td>7&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Tambe and Bhushan (2005g); <sup>b</sup>Kasai et al. (2005); <sup>c</sup>Lee et al. (2005)

Table 4.3: Film thickness of various SAMs.
Figure 4.11 (a) shows the relationship between the decrease in surface height corresponding to an increase in the normal load as found for various SAMs during wear tests. As shown in the figure, the SAMs exhibit a critical normal load beyond which point the surface height drastically decreases. Figure 4.11 (a) also shows the wear behaviors of the Al and Si substrates. Unlike the SAMs, the substrates show a monotonic decrease in surface height with the increasing normal load with wear initiating from the very beginning, i.e. even for low normal loads. Si (Young’s modulus of elasticity, $E=130$ GPa (Anonymous, 1988), hardness, $H=11$ GPa (Bhushan, 1999c)) is relatively hard in comparison to Al ($E=77$ GPa, $H=0.41$ GPa (Wei, 2004)) and hence the decrease in surface height for Al is much larger than that for Si for similar normal loads.

The critical loads corresponding to the sudden failure of SAMs are shown in Fig. 4.11 (b). Amongst all the SAMs, OP and ODP show the best performance in the wear tests. Out of the two, ODP shows higher critical load and this is believed to be because of the chain length effect (Kasai et al., 2005). Fluorinert has much higher film thickness to start with in comparison to PFPTES (see Table 4.3) and hence shows a higher critical load to failure. AFM images of the Fluorinert samples taken after the wear tests revealed agglomeration of the lubricant molecules in the “wear” area suggesting that the mobile fraction of molecules of Fluorinert can get displaced from under the tip while sliding but “flow” back once the tip has slid past. Thus the critical load in this case is higher as the lubricant mobility ensures that the substrate is not exposed easily.

Bhushan and Liu (2001) and Liu and Bhushan (2002b) have explained the mechanism of failure of compliant SAMs during wear tests. Figure 4.12 schematically illustrates the stages proposed by them during the wear of SAMs. It is believed that the SAMs fail mostly
Figure 4.11: (a) Decrease in surface height as a function of normal load after one scan cycle and (b) Comparison of critical loads for failure during wear tests for various SAMs

(Tambe and Bhushan, 2005g)
due to shearing of the molecule at the head group, that is, by means of shearing of the molecules off the substrate. The weakest bonds are at the interface (see Table 4.4) and hence failure is expected to be initiated at the interface. Based on the investigations of the different kind of SAMs, their nanotribological properties can be summarized as shown in Table 4.5.

Figure 4.12: Schematic illustrating wear mechanism of SAMs (Tambe and Bhushan, 2005g, first proposed by Bhushan and Liu, 2001)
<table>
<thead>
<tr>
<th>SAMs</th>
<th>Bond strengths (kJ/mol)</th>
<th>Diatomic strength $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP and ODP</td>
<td>Al – O</td>
<td>511</td>
</tr>
<tr>
<td></td>
<td>P – O</td>
<td>599</td>
</tr>
<tr>
<td></td>
<td>P – C</td>
<td>513</td>
</tr>
<tr>
<td>PFPTES</td>
<td>Si – O</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Si – C</td>
<td>451</td>
</tr>
</tbody>
</table>

$^a$ Lide (2004)

Table 4.4: Bond strengths of various chemical bonds in the SAMs (It should be noted that the bond strengths for SAMs resulting from chemical adsorption on the corresponding substrates are expected to be lower than the diatomic strengths).

<table>
<thead>
<tr>
<th>SAMs property</th>
<th>Friction force</th>
<th>Adhesive force</th>
<th>Wear</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Soft</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Chemical structure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear chain molecule</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Ring molecule</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Backbone</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorocarbon backbone</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Hydrocarbon backbone</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Chain length</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long backbone chain</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Short backbone chain</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

Table 4.5: Summary of nanotribological characterization studies for SAMs on Si and Al substrates
4.4 Closure

Initiation of wear was studied for various materials, coatings and lubricants. At high velocities, deformation of contacting asperities from the high velocity impacts was found to result in high friction for most of the samples. Si (100) showed the poorest durability and this is believed to be the result of a combination of: deformation resulting from impacts of the contacting asperities and the corresponding three-body wear due to debris particles generated at the sliding interface and a tribochemical reaction which is accelerated by high velocities. For DLC the high energy dissipation results in phase transformation to a low shear strength graphite-like layer at the sliding interface which has low friction, hence DLC shows higher durability. At higher normal loads, however, the graphite-like debris can get ejected from the interface and increase friction. For the lubricants HDT, Z-15 and Z-DOL, durability was governed by the displacement of the mobile molecules or the removal of the bonded molecules from the sliding interface. For the polymers PMMA and PDMS, durability was governed by localized melting of the contact zone due to high energy dissipation. These results help explain the nanoscale wear mechanisms for various materials, coatings and lubricants that have wide applications in MEMS/NEMS.

A novel AFM based approach for nanowear mapping was developed. The technique, based on simultaneous controlled movements of the sample and AFM tip, provides a fast and efficient means for mapping the sample surface wear as a function of the sliding velocity, the applied normal load and the number of sliding cycles. Nanoscale wear maps revealed drastic and sudden failure in case of Si (100) resulting from two- and three-body abrasive wear from asperity impacts at high sliding velocities. For DLC wear
debris was generated as a result of phase transformation of DLC to a graphite-like phase. A nanowear map generated on DLC by simultaneously varying sliding velocity and the normal load revealed this very well.

The ability to achieve high sliding velocities that are close to those of engineering interest in conjunction with the novel approach developed for studying nanoscale wear can be adapted very easily to study any materials, coatings and lubricants and the nanoscale wear can be mapped in a fast and efficient manner. By appropriate selection of operating parameters, wear maps can be obtained to reveal the competing wear mechanisms. This technique can have a very promising role to play in evaluating potential materials for MEMS/NEMS applications. It should however be noted that wear is not always a result of abrasion or cracking and may not necessarily show up in the form of visible wear debris. The conventional AFM is limited when mapping wear that does not result in visible debris generation. Other AFM based techniques have to be then incorporated such as those which map the change in surface potential as a wear precursor [DeVecchio and Bhushan, 1998; Bhushan and Goldade, 2000a, b].

So far in this dissertation the velocity dependent nature of friction, adhesion and wear was investigated. However it is known that often tribological and mechanical properties exhibit a scale dependent nature, i.e. they differ on macro-, micro- and nanoscale. Understanding this dependence is critical to the materials selection process in the design and development of nanotechnology applications. In the next chapter this scale dependent nature of friction and adhesion is discussed.
CHAPTER 5
SCALE DEPENDENCE OF MICRO/NANOSCALE FRICTION AND ADHESION

Miniaturization of components and devices and the rapid development of MEMS/NEMS and various biomedical applications (BioMEMS/NEMS) have resulted in a plethora of nanotechnological applications (Bhushan, 2004). However, there has been only limited progress in gaining a sound understanding of materials behavior on the micro/nanoscale. Many studies have shown a strong size or scale dependence for mechanical properties such as indentation hardness (Bhushan and Koinkar, 1994; Bhushan and Kulkarni, 1996; Bhushan et al., 1996; Bhushan, 1998, 1999a, d, e, 2004; Nix and Gao, 1998; Hutchinson, 2000), tensile strength (Hutchinson, 2000) and bending strength (Sundararajan and Bhushan, 2002) indicating that the bulk properties of many materials differ from those on the micro/nanoscales. The scale-invariance of the theory of linear elasticity and the conventional plasticity theories has led to the formulation of a new theory, the strain gradient plasticity theory (Fleck et al., 1994; Nix and Gao, 1998; Gao et al., 1999; Huang et al., 2000; Hutchinson, 2000). The theory, developed for microscale deformation, predicts a dependence of mechanical properties on the strain gradient which is scale dependent.

Micro/nanotribological studies become important as device size shrinks and surface forces such as adhesion and friction become dominant over the inertial and
gravitational forces due to large surface area to volume ratios (Tas et al., 1996; Bhushan, 1998, 2003, 2004; Mastrangelo, 1998; de Boer and Mayer, 2001; Tang and Lee, 2001; Komvopoulos, 2003). The fundamental laws of friction as stated by Amontons and Coulomb have been known to no longer hold on the micro/nanoscales and studies have shown that tribological properties such as coefficient of friction and wear rates can be different on nanoscale than on macroscale (Bhushan et al., 1995; Bhushan and Kulkarni, 1996; Bhushan, 1999a, d, 2004). Recently the strain gradient plasticity theory has been used for modeling the scale effects in friction and wear (Bhushan and Nosonovsky, 2003, 2004a, b; Nosonovsky and Bhushan, 2005).

A comprehensive micro/nanotribological characterization of the scale dependent nature of materials properties is of paramount importance, not only for the design of reliable industrial applications but also to provide a bridge between science and engineering on the micro/nanoscale. Nosonovsky and Bhushan (2005) have presented a theoretical analysis of the scale effects in dry friction for multiasperity contacts. Bhushan et al. (2004) and Tambe and Bhushan (2004b) have presented an experimental investigation of the scale dependence of micro/nanotribological properties. The nanoscale experiments were conducted on the modified AFM setup (Tambe and Bhushan, 2005a) using square pyramidal Si$_3$N$_4$ tips with nominal radii 30-50 nm, mounted on gold coated triangular Si$_3$N$_4$ cantilevers having a nominal spring stiffness of 0.58 N/m. Microscale experiments were conducted using a microtriboapparatus (Tetra Inc., Ilmenau, Germany). Experiments were run using a single crystal Si (100) ball mounted on a stainless steel cantilever having a stiffness of 57 N/m along the normal load axis. The 1 mm diameter, $5\times10^{17}$ atoms/cm$^3$ boron doped balls were obtained from Ball Semiconductor Inc., Allen,
TX, USA. The detailed description and working of the instrument as well as the calibrations of the cantilever etc can be found in Liu and Bhushan (2003b).

Contact angle, which is a measure of surface hydrophobicity, was measured using a Rame-Hart model 100 contact angle goniometer. Demineralized distilled water droplets were used for making contact angle measurements. The measurements were done at 20±2 °C and 50±5 % RH and were reproducible to within ±2°. Environmental studies were performed by controlling the humidity and temperature. Adhesive force was measured at different relative humidity between 0 % and 80 % and at different temperatures between 20 °C and 125 °C.

5.1 Scale dependence of micro/nanoscale friction and adhesion

MEMS/NEMS and BioMEMS/NEMS devices are designed for operation under various operating parameters and environmental conditions and can have surface contacts which are either point or line contacts as for example between the meshing teeth in a microgear set or area contacts as for example between the mirror and the landing site in digital micromirror devices (Bhushan, 2004). The interaction between the asperities on these contacting interfaces is governed by surface forces and the resulting adhesion originating from a number of attractive and/or repulsive forces including van der Waals and electrostatic, and dynamic interactions due to hydrodynamic, viscous, and lubrication forces (Zhao et al., 2003; Bhushan, 2004). Surface hydrophobicity is also an important property as it determines the strength of the adhesive interaction between sliding surfaces resulting from meniscus bridge formation (Bhushan, 2003; Bhushan et al., 2004). Contact angle, which is a measure of surface hydrophobicity, is roughness dependent (Wenzel,
1936) and roughness in turn is a scale dependent property. The important tribological properties that are investigated in this study include the adhesive force and friction force dependence on operating parameters such as rest time and sliding velocity and environmental conditions such as relative humidity and temperature.

5.1.1 Asperity size (roughness) dependence of friction

In Fig. 5.1 (a) we present friction data measured for different scan sizes between 2 and 25 µm and over a range of sliding velocities using Si (100) sample and Si3N4 tip. The friction force was found to be higher for larger scan sizes at all velocities. Moreover, the trend lines shown for all scan sizes are mutually parallel, indicating that the scan size dependence of friction force was independent of the sliding velocity. The friction force increases nearly linearly with scan size and this trend is similar to that reported by Koinkar and Bhushan (1997) for Si (100) sample for scan sizes greater than 1 µm. The reason for such dependence is the scale dependent nature of the roughness of the sample surface. Figure 5.1 (b) shows AFM topography images and 2D cross sectional profiles of the Si (100) sample surface measured for different scan sizes. A simple model is described next to relate the roughness of the sample surface to the scan size dependence of friction force.

Consider an AFM tip sliding past the sample surface (see Fig. 5.1 (b)) with normal load, W, and instantaneous friction force, F, owing to inclination, θ, of the sample surface at a given location. The directions of the local normal reaction, N, and the
Figure 5.1: Friction force dependence on scan size. Measurements at different velocities indicate that the scan size dependence of friction force is independent of the effect of the scanning velocity (Tambe and Bhushan, 2004b). AFM images and 2D cross section profiles at different scan sizes for Si (100) sample surface and analytical model showing scan size dependence of friction force. The roughness parameters, standard deviation ($\sigma$) and peak to valley distance (P-V) are indicated along the respective AFM images. The values are averaged over the entire scan size and were obtained using commercial AFM software (Tambe and Bhushan, 2004b)
Figure 5.1 continued

AFM images at different scan sizes for Si (100) with native SiO₂

\[
\sigma = 0.4 \text{ nm} \\
P - V = 3.2 \text{ nm}
\]

\[
\sigma = 0.58 \text{ nm} \\
P - V = 31 \text{ nm}
\]

\[
\sigma = 1.1 \text{ nm} \\
P - V = 58 \text{ nm}
\]

Instantaneous friction force at the AFM tip-sample interface is a function of the surface slope (θ) at that location.

\[
\mu = \frac{F}{W} \quad \text{and} \quad \mu_0 = \frac{S}{N}
\]

\[
\mu_1 = \mu_0 + \tan \theta
\]

For small surface inclinations, θ

\[
\mu_1 = \mu_0 + \theta
\]

The average friction force is

\[
F_{avg} = \frac{\theta_2}{\theta_1} \int_{\theta_1}^{\theta_2} (\mu_0 + \theta) W d\theta
\]

or \( F_{avg} \propto (\theta_2 - \theta_1) \)

The friction force \( F \) scales with the scan size.
instantaneous local resistance to motion, $S$, are shown in the schematic. In such a case the
instantaneous value of the local coefficient of friction, $\mu_1$, and the constant value of the
coefficient of friction, $\mu_0$, can be given by following equations

$$
\mu_1 = \frac{F}{W} \quad \text{and} \quad \mu_0 = \frac{S}{N}
$$

(42)

For a tip ‘riding up’ on the sample surface, it can be shown that for small values of
surface inclinations, $\mu_1$ and $\mu_0$ are related by the following equation

$$
\mu_1 = \frac{\mu_0 + \tan \theta}{1 - \mu_0 \tan \theta}
$$

(43)

and for small values of surface inclination, $\theta$, we have

$$
\mu_1 \approx \mu_0 + \theta
$$

(44)

Thus the instantaneous friction force can be written as

$$
F = (\mu_0 + \theta)W
$$

(45)

For simplicity we can consider a surface with repeated surface roughness with known
periodicity. The AFM images in Fig. 5.1 (b) indicate that the silicon surface does exhibit
such a periodic roughness. The average friction force encountered by the tip as it slides
between two given points on the sample surface is

$$
F_{\text{avg}} = \frac{\int_{\theta_1}^{\theta_2} F(\theta)d\theta}{\theta_2 - \theta_1}
$$

(46)

where $\theta_1$ and $\theta_2$ are the surface inclinations at two extreme locations on the tip scan path
while the tip is riding up the surface and thus the difference $(\theta_2 - \theta_1)$ is a reflection of the
scan size. For larger scan sizes, when the tip has to ride up and down the surface, the
integral limits in eq. (43) change accordingly and the friction force becomes additive in nature. Substituting eq. (45) in eq. (46) we get the following expression

\[ F_{\text{avg}} = \frac{\int_{\theta_1}^{\theta_2} (\mu_0 + \theta) W d\theta}{\theta_2 - \theta_1} = \mu_0 W + \frac{1}{2} (\theta_2 + \theta_1) W \]  

(47)

Thus we have the relation

\[ F_{\text{avg}} \propto (\theta_2 + \theta_1) \]  

(48)

For a given initial location \( \theta_1 \), as the scan size is changed, \( \theta_2 \) changes and correspondingly the friction force changes linearly with it.

For exploring the scale dependent nature of coefficient of friction, experiments were conducted on the micro- and nanoscale. The values obtained on the nanoscale using the Si\(_3\)N\(_4\) tip and on the microscale using the Si (100) ball for various samples are listed in Table 5.1. The coefficient of friction was found to be significantly higher on the microscale than on the nanoscale. The scale dependence of the coefficient of friction in this case is believed to be a combination of two independent factors, the scan size and the tip (or ball) radius or to be more specific the size of the asperities encountered during sliding. Previous studies have shown that coefficient of friction increases with an increasing tip radius (Bhushan and Sundararajan, 1998). For larger scan size and larger tip radius, the surface interaction is not limited to nanoscale asperities but microscale asperities influence the friction as well. Bhushan and Nosonovsky (2004a, b) and Nosonovsky and Bhushan (2005) give a comprehensive model for the scan size dependence of friction force and show that for multiple-asperity elastic contacts the
coefficient of friction increases with scale while for plastic contacts it either increases or decreases with scale depending on the material properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nanoscale (2 ( \mu \text{m} ) scan size, 4( \mu \text{m/s} ))</th>
<th>Microscale (1000 ( \mu \text{m} ) scan size, 720( \mu \text{m/s} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adhesive force (nN)</td>
<td>Coefficient of friction</td>
</tr>
<tr>
<td>Si (100)</td>
<td>50</td>
<td>0.05</td>
</tr>
<tr>
<td>DLC</td>
<td>40</td>
<td>0.03</td>
</tr>
<tr>
<td>HDT</td>
<td>17</td>
<td>0.02</td>
</tr>
<tr>
<td>Z-DOL</td>
<td>35</td>
<td>0.03</td>
</tr>
<tr>
<td>Z-15</td>
<td>84</td>
<td>0.01</td>
</tr>
<tr>
<td>PMMA</td>
<td>26</td>
<td>0.06</td>
</tr>
<tr>
<td>PDMS</td>
<td>190</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Tables 5.1: Scale dependence of coefficient of friction and adhesive force
5.1.2 Rest time dependence of adhesive force on micro and nanoscale

Figure 5.2 shows the adhesive force values on both the micro- and nanoscales for various samples. The adhesive force values are also summarized in Table 5.1. Adhesive force arises from the presence of a thin liquid film such as a mobile lubricant or adsorbed water layer that causes meniscus bridges to build up around the contacting and near contacting asperities as a result of surface energy effects. The attractive meniscus force arises from the negative Laplace pressure inside the curved menisci and is given by the product of this pressure difference and the immersed surface area of the asperity. This intrinsic attractive force may result in high friction and wear (Bhushan, 2003). The total meniscus force, $F_m$, at the sliding interface is obtained by summing the meniscus forces from all individual contacting and non-contacting asperities where menisci bridges are formed (Bouquet et al., 1998; Chilamakuri and Bhushan, 1999) and is given by the equation (5). Unless the surface is covered with a liquid film (as is the case with the mobile lubricant molecules of Z-15 used in our study), the surface hydrophobicity dictates the meniscus bridge formation at the interface. Contact angle is a direct measure of the surface hydrophobicity and depending upon whether the contact angle is $<90^\circ$ or $>90^\circ$ the surface can be termed as hydrophilic or hydrophobic.

Figure 5.2 also gives the contact angles for all the samples along with the calculated Laplace force. For larger contact angles, i.e. higher hydrophobicity, the Laplace force is lower and the corresponding measured adhesive force values are also lower as expected. Since we calculate the Laplace force assuming a single asperity contact (i.e. $N(t)=1$) there is some disparity seen in the calculated and measured values. The disparity is much higher for Z-15 and PDMS as compared to other samples. In case
Figure 5.2: Contact angle for various samples and the corresponding values of the calculated Laplace force and the measured adhesive force. The samples are ranked in the order of decreasing contact angle (or increasing degree of surface hydrophobicity) from left to right (Tambe and Bhushan, 2004b)
of Z-15, the lubricant molecules are mobile and can form meniscus bridges at the interface. Their contribution is not included in our calculations for the Laplace force. In case of PDMS, the disparity is the result of various other forces such van der Waals and electrostatic that contribute to the adhesive force. PDMS is a very soft polymer and the sample conforms to the tip (or ball) more readily than other samples. This increases the real area of contact and results in higher adhesion (Moore, 1972). PDMS was also found to exhibit long range attraction during nanoscale measurements due to electrostatic surface charge. The Si (100) ball cantilever with higher stiffness than the Si$_3$N$_4$ cantilever did not detect the relatively weak electrostatic force of attraction. This scale dependent nature is a good indication of how surface forces such as electrostatic attraction that are relatively weak on the microscale can become humongous on the nanoscales and result in high adhesion.

A comparison of the calculated Laplace force values and the measured adhesive force values (see Fig. 5.2) shows that both the calculated and measured values are higher on the microscale as compared to the nanoscale. From equation (5) we note that Laplace force depends on the radius of tip (or ball) and since the ball radius of 0.5 mm was larger than the tip radius of 50 nm the calculated values are higher on the microscale. The reason for higher adhesive force on the microscale is that more asperities come in contact for the ball-sample interface than for the tip-sample interface. Also it should be noted that measurements on the microscale were performed with Si (100) ball while on the nanoscale they were performed with a Si$_3$N$_4$ tip with different roughness distributions and some disparity in the results should be expected owing to this.
Apart from this the scale dependent nature of contact angle can also contribute to the higher adhesive forces on the microscale than on the nanoscale. Contact angle is known to be dependent on sample surface roughness (Wenzel, 1936; Nosonovsky and Bhushan, 2004) which in turn is a scale dependent property. For this study, however, the contact angle was assumed to be the same on the micro- and nanoscale.

The adhesive force measurements and the corresponding Laplace forces provide an insight into the contribution of meniscus force for various samples. The adhesive force between surfaces that are in contact is known to increase rapidly with rest time as more meniscus bridges build up at the contacting and near-contacting asperities and the resulting high adhesion is a critical failure issue encountered in fabrication as well as regular operation of many MEMS/NEMS components (Bhushan, 1998, 2003). Figure 5.3 gives the rest time dependence of adhesive force for all the samples on the micro- and nanoscale. Only Si (100), which is hydrophilic, and Z-15, with mobile lubricant molecules, show any rest time dependence. The adhesive force is found to increase with rest time for these samples and then level off at high rest times. This increase has been shown to be logarithmic in nature (Bouquet et al., 1998; Chilamakuri and Bhushan, 1999). The rest of the samples are either partially or completely hydrophobic and show negligible or no rest time dependence. The adhesive force measured on the microscale is high as compared to that measured on the nanoscale and as explained earlier is a result of the larger radius of the silicon ball as compared to the AFM tip radius.
Figure 5.3: Rest time dependence of adhesive force for all samples on the micro- and nanoscale (Tambe and Bhushan, 2004b)
5.1.3 Environmental effects: Relative humidity (RH) and temperature dependence of adhesive force on the micro and nanoscale

The influence of RH and temperature for all the samples on both the micro- and nanoscale is presented in Figs. 22 and 23. The behavior is very similar on both the scales, in the sense that the samples which show a RH or temperature dependence on nanoscale also show a similar dependence on the microscale. DLC, Z-DOL and Z-15 are partially hydrophobic while silicon is the most hydrophilic of all samples studied. At higher RH and lower temperatures, more water molecules can condense on the sample surface resulting in higher adhesive forces. At higher temperatures desorption of water molecules and the reduction of surface tension of water (Lide, 1994) results in a decrease in adhesive force. HDT and PMMA which have highly hydrophobic surfaces show no RH or temperature dependence. In case of PDMS, the adhesive force is found to slightly drop at very high humidity for the nanoscale tests and at high temperatures for the microscale tests. Since the adhesion for PDMS on the nanoscale is largely due to the electrostatic attraction the drop in adhesive force is most probably the result of weakening of the electrostatic charge. It is known that the effect of static electric surface charge diminishes at higher humidity (Einstein, 1967). At high temperatures, the adhesive force for PDMS is found to drop for tests on both the micro- and nanoscales. Such a dependence of the adhesive force on temperature is well known for viscoelastic polymers and various theories have been proposed to explain this dependence (Moore, 1972).
Figure 5.4: Relative humidity dependence of adhesive force for all samples on the micro- and nanoscale (Tambe and Bhushan, 2004b)
Figure 5.5: Temperature dependence of adhesive force for all samples on the micro- and nanoscale (Tambe and Bhushan, 2004b)
5.1.4 Velocity dependence of friction and adhesion on the micro and nanoscale

Figure 5.6 shows the velocity dependence of friction force for both the micro- and nanoscale measurements. The results show remarkable similarity in the trends for some of the samples while they are distinctly different for the other samples. The velocity dependence of friction force for Si (100) and Z-15 is predominantly governed by the meniscus force contributions (Koinkar and Bhushan, 1996; Liu and Bhushan, 2003a, b). The meniscus force however is scale dependent and hence the friction force is higher on microscale as compared to that on the nanoscale. At high velocities the meniscus force loses its dominance as there isn’t sufficient time available for stable meniscus formation at the contacting asperities. Since the range of velocities investigated on the microscale was lower than those on the nanoscale this particular behavior was not seen for microscale experiments.

For DLC, velocity dependence of friction force on the nanoscale is governed by atomic scale stick-slip (Riedo et al., 2003) at low velocities and phase transformation of DLC to graphite-like low shear strength layer by a sp$^3$ to sp$^2$ phase transition (Voevodin et al., 1996; Grill, 1997; Tambe and Bhushan, 2005e) at high velocities. The sharp Si$_3$N$_4$ tip used in AFM studies (30-50 nm radius) gives rise to contact pressures in the range of 1.8-3.8 GPa for DLC films corresponding to normal loads of 10-100 nN (Tambe and Bhushan, 2005e) and Voevodin et al. (1996) have reported formation of debris with polycrystalline graphite like structure for contact pressures in the range of 0.8-1.1 GPa. At high velocities, the high contact pressures combined with the frictional energy dissipation due to asperity impacts and the associated temperature rise at the contacting asperities on the tip-sample interface will accelerate the phase transformation process.
Figure 5.6: Velocity dependence of adhesive force for all samples on the micro- and nanoscale (Tambe and Bhushan, 2004b)
From our experimental results we find that DLC shows no velocity dependence on microscale. For experiments conducted on the microscale, the large radius of the Si (100) ball implies that there is no atomic-scale stick slip involved as only the larger asperities can come into contact. Moreover, the contact pressure for Si (100) ball on DLC is very low, about 0.162 GPa (Bhushan et al., 2004). Thus phase transformation of DLC might not occur even at high velocities on the microscale. This explains the velocity independence of DLC on the microscale.

In case of HDT, the friction force dependence on velocity is attributed to the molecule reorientation. As the tip slides past the compliant HDT molecules, they reorient in the sliding direction and restrict tip motion when the tip returns on its reverse scan path leading to high friction. At higher velocities, however, the molecules do not have sufficient time for reorientation (Joyce et al., 1992) and hence friction force stabilizes at a steady value. Since the tip radius is smaller than the ball radius by almost four orders of magnitude the microscale measurements do not show similar behavior. For Z-DOL, the friction force starts to increase at relatively lower velocities on the nanoscale than those on the microscale. This is believed to be due to a combination of larger energy dissipation from the tip impacts and comparatively higher contact pressures on the nanoscale (Bhushan et al., 2004).

For the partially hydrophobic PMMA, the primary friction mechanism is stick-slip at low velocities and deformations of contacting asperities from impacts at high velocities. The behavior is thus very similar on both micro- and nanoscale. The friction force is higher due to the scale dependent nature of surface roughness. PDMS on the other hand is softer and can absorb most of the impacts even at high velocities. The
primary contribution to friction for PDMS is the stick-slip resulting from the high adhesion of sliding interface and energy is dissipated mainly due to deformation hysteresis. Velocity dependence of viscoelastic polymers such as PDMS has been studied on the macroscale and is well documented (Moore, 1972). On the nanoscale, apart from the sample-tip interfacial adhesion, the electrostatic attraction also contributes and results in high adhesion. With increasing velocity the stick-slip component diminishes and friction reduces.

Overall the velocity dependence results for friction force indicate strong scale dependence. The scale dependent nature of sample surface roughness, the high contact pressures and higher adhesion on the nanoscale are the primary reasons for the scale dependence of friction force at different sliding velocities. This emphasizes the fact that in designing micro/nanoscale devices the friction force dependence of velocity for one scale cannot be assumed to hold on another scale for the same sliding interface materials.

5.2 Implications of the scale dependence of micro/nanotribological properties

The scale dependence of friction force and the coefficient of friction was found to be the result of two independent factors, the scan size and the tip radius (or ball radius) or more specifically the size of the contacting asperities. For larger scan sizes and larger asperity sizes the coefficient of friction was significantly higher. The contact angle is known to be roughness dependent which in turn is a scale dependent property. The results indicate that the calculated Laplace force values and the measured adhesive force values on both the micro- and nanoscale are close for most samples but show no specific trend that can help deduce the scale dependence of the contact angle. In case of PDMS, the
contribution of electrostatic attraction to the total adhesive force was large on the nanoscale but it was negligible on the microscale. Rest time, relative humidity and temperature dependence of adhesive force on the micro- and nanoscale was primarily the result of the scale dependent nature of the meniscus force and the sample surface roughness. The adhesive force was always found to be higher on the microscale than on the nanoscale. The velocity dependence of friction force showed significant scale dependence for some samples. The primary reason for this scale dependence is the sample surface roughness and the higher contact pressures that are encountered on the nanoscale.

The scale dependence study emphasizes the importance of the investigations of the scale dependence of micro/nanotribological properties to the design of micro/nanoscale devices.
CHAPTER 6

IMPACTS OF NANOTRIBOLOGICAL INVESTIGATIONS AT HIGH SLIDING VELOCITIES FOR NANO TECHNOLOGY APPLICATIONS

Nanotribological investigations conducted for various materials, coatings and lubricants that are considered as potential solutions for nanotechnology applications at high sliding velocities have encompassed velocity regimes of scientific as well as engineering interest thereby enabling development of a broader and more fundamental understanding of the nanoscale friction behavior. The comprehensive analytical friction model explains friction behavior scaling multiple regimes and also helps identify the critical parameters corresponding to transitions between various friction regimes. The scale dependence of micro/nanotribological properties reveals the primary reasons for the scale dependence are the sample surface roughness, the asperity sizes and the contact pressures. The scale dependence study emphasizes the fact that material behavior on one scale cannot be assumed to hold on another scale. The results signify the importance of the study of micro/nanotribological properties to the design of micro/nanoscale devices. At the same time it brings out the necessity to investigate material properties on the scales that are most pertinent to and the sliding velocities that correspond to those found in most real world applications when designing micro/nanostructures and devices. In the next sections the significance of the research discussed in this dissertation to
nanotechnology applications, their design and development is discussed in detail. Various materials, coatings and lubricants that were investigated as part of this dissertation are ranked on the merits of tribological properties. A Young’s modulus dependence on friction and adhesion that enables materials selection for specific applications based on their tribological properties such as low friction and adhesion is discussed. Lastly, the attractive use of DLC as a protective coating for nanotechnology applications is explored.

6.1 Significance to design of nanotechnology applications

Nanotribological investigations at high sliding velocities were expected to provide not only a fundamental understanding for behavior of these materials as individual entities but also give a bigger picture that is necessary for developing newer, better and longer lasting solutions for the next generation nanodevices that are more reliable and efficient.

Figure 6.1 provides a “superiority index” prepared on the basis of a weighted point average method. The properties of interest considered here are the surface hydrophobicity which pertains to the degree of adhesion expected from meniscus contributions; the actual adhesive force measured which is an indicator of any potential problems posed by the particular sample in consideration, the coefficient of friction which is a indicator of the amount of energy or work that needs to be put into a specific system to keep it running or from thermodynamics point of view the amount of energy lost in making a system to simply work or deliver the expected output; the durability which is a indicator of the lifetime of a particular device or component and the velocity dependent friction force which governs the working of a wide array of applications with parts that have relative sliding motion involved. The index is based on a non-scientific manner of
Figure 6.1: Relative ranking of various MEMS/NEMS materials, coatings and lubricants based on their micro/nanotribological characterization studies (Note: Higher the index value, superior is the sample)
comparison where each material is assigned low points for the worst performance in each category. The net sum of points ascertained from all properties is then charted to give the superiority index. This method though not scientifically accurate proves to be a fruitful endeavor here since the samples being tested cover a wide range of material properties. Moreover the results follow those reported before by researchers (Grill, 1997; Bhushan, 1999c; Sundararajan and Bhushan, 2001; Liu and Bhushan, 2003a; Bhushan et al., 2004; Bhushan 2004; Tambe and Bhushan, 2005e).

The chart shows that the most superior behavior is shown by HDT which is a self-assembled monolayer. Self-assembled monolayers are considered to be the ultimate solutions in thin film lubrication (Ulman, 1991; Bhushan, 2004). Z-DOL which is a bonded layer of perfluoropolyether molecules is well known lubricant owing to its excellent stability to thermal as well as oxidative degradation apart from tribological considerations and is a widely used lubricant in the magnetic data storage industry (Bhushan, 1996). Its use for MEMS/NEMS has been investigated (Sundararajan and Bhushan, 2001; Liu and Bhushan, 2003a) before and promising results have been predicted. DLC is the third best on the index and is a very promising protective coating for high speed nanoscale devices and components. DLC has been shown to be an excellent alternative as a low friction and adhesion coating (Grill, 1997; Bhushan, 1999c; Bhushan et al., 2004; Tambe and Bhushan, 2005e). It is already widely used in the hard disk drive and magnetic tape industry as a protective coating (Bhushan, 1996).

Figure 6.2 schematically summarizes the impact of nanotribological investigations at high sliding velocities for nanotechnology applications. Fundamental studies can be conducted by emulating the nanoscale contacts using an AFM. New
techniques developed for high speed scanning allow for investigating friction behavior at sliding velocities that are pertinent to operation of many real world micro/nanodevices and components such as the microgear drive (Fig. 6.2). By developing a fundamental understanding of the failure mechanisms involved various materials, coatings and lubricants can be evaluated for incorporation into future design and development of nanotechnology applications.

6.2 Materials selection aspect of nanotechnology applications

Other than tribology, mechanics on the nanoscale has been shown to be the most significant field of study for the design of reliable and failure-proof micro/nano devices for various nanotechnology applications. The interdependence between friction and material properties is of significant interest for selecting materials that would be ideal from tribology point of view, i.e. materials with low friction and adhesion. Scientific studies indicate that mechanical properties can strongly affect the tribological performance (Bhushan, 1999b). Efforts to explicitly characterize the nanoscale friction and adhesion of various materials on the basis of their mechanical properties remain limited though. Recently Tambe and Bhushan (2005f) have established a vital link between the Young’s modulus of materials and the coefficient of friction and adhesion over a range of sliding velocities.

Table 6.1 lists the materials used in this study along with their Young’s modulus and the corresponding coefficient of friction values. Also listed are the materials studied by previous researchers under identical experimental and environmental conditions. In case of the materials for which a range of values has been reported for the coefficient of
Figure 6.2: Utility and impact of nanotribological investigations conducted at high sliding velocities on future design of MEMS/NEMS and other nanotechnology applications.
friction, the average values are listed. Hence forward in this chapter materials with lower Young’s modulus are referred to as low E materials and those with higher Young’s modulus are referred to as high E materials.

A clear trend was found for the coefficient of friction dependence on the Young’s modulus (Fig. 6.3). (It has to be noted that the sliding interface will only undergo elastic deformations under the very low normal loads used in the experiments.) Low E materials show higher coefficient of friction as compared to the high E materials. This result can be intuitively inferred from the classical theories of friction (Bowden and Tabor, 1964; Persson, 2000; Bhushan, 1999b). An approximate relation can be developed between the coefficient of friction and the Young’s modulus by assuming a single-asperity elastic contact and using Hertzian contact analysis. For most sliding interfaces though, the contact is often a multi-asperity contact and no closed form analytical solutions exist. Numerical methods have to be employed for solving problems dealing with multi-asperity contact (Bhushan, 1999b). Moreover nanoscale friction and adhesion is largely dependent on sample surface roughness and the shear strength of the sliding interface (Persson, 2000; Bhushan, 1999b). Table 6.1 indicates that the roughness values of the samples are not the same, although they are comparable. In light of this limitation on analytical formulations and the inherent complexity involved in relating the nanoscale friction and adhesion to the material properties, the near logarithmic dependence of the coefficient of friction on the Young’s modulus shown by a wide variety of materials in the experimental data is extremely interesting. Only highly oriented pyrolytic graphite (HOPG) stands out as an anomaly in this trend and this is because of its extremely low shear strength.
<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
<th>Ref.</th>
<th>Coefficient of friction</th>
<th>RMS roughness (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>1140</td>
<td>[1]</td>
<td>0.05</td>
<td>2.3</td>
<td>[8]</td>
</tr>
<tr>
<td>SiC</td>
<td>395</td>
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<td>0.02</td>
<td>0.89</td>
<td>[2]</td>
</tr>
<tr>
<td>DLC</td>
<td>280</td>
<td>[3]</td>
<td>0.03</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Si (111)</td>
<td>188</td>
<td>[4]</td>
<td>0.04</td>
<td>0.14</td>
<td>[8]</td>
</tr>
<tr>
<td>Polysilicon</td>
<td>167</td>
<td>[2]</td>
<td>0.04</td>
<td>0.86</td>
<td>[2]</td>
</tr>
<tr>
<td>Si (100)</td>
<td>130</td>
<td>[4]</td>
<td>0.05</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Al alloy film</td>
<td>91</td>
<td>[5]</td>
<td>0.06</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Au (111)</td>
<td>77</td>
<td>[6]</td>
<td>0.035</td>
<td>0.37</td>
<td>[11]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>73</td>
<td>[7]</td>
<td>0.05</td>
<td>0.14</td>
<td>[8]</td>
</tr>
<tr>
<td>HOPG</td>
<td>9-15</td>
<td>[1]</td>
<td>0.008</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>7.7</td>
<td>[9]</td>
<td>0.07</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>PDMS</td>
<td>0.36-0.87</td>
<td>[10]</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table 6.1: Young’s modulus (E) and measured values of coefficient of friction. All measurements were performed using Si₃N₄ AFM tips of nominal radius 30-50 nm in controlled environment of 20±2 °C and 50 % RH.
Figure 6.3: Coefficient of friction dependence on the Young’s modulus for various materials. Measurements were made using Si$_3$N$_4$ AFM tips of nominal radius 30-50 nm in controlled environment of 20±2 °C and 50 % RH (Tambe and Bhushan, 2005f).
Figure 6.4 shows the velocity dependence of adhesion and the coefficient of friction over a range of velocities for different materials. The contour maps (Fig. 6.4) give the Young’s modulus dependence of these two quantities for the same materials. Some very interesting trends are revealed by the contour maps. Adhesion is high for low E materials and at low sliding velocities and it gradually decreases with an increase in velocity. The velocity dependence of friction and adhesion in case of viscoelastic polymers (such as PDMS used in this study) is well known and it is defined by a definite peak occurring at a specific sliding velocity (Moore, 1972; Persson 2000; Bhushan, 1999b). Similar behavior was found even in the case of materials with higher Young’s modulus where the adhesive force increased with velocity and reached a peak. Moreover the peak was attained at higher velocities for materials with higher E value. The contour map for coefficient of friction also reveals peculiar trends. At low velocities, the coefficient of friction decreases with increasing Young’s modulus and this decrease is found to be nearly logarithmic in nature (seen from Fig. 6.3). However at high velocities this trend is reversed and the coefficient of friction is found to increase with increasing Young’s modulus. At high velocities friction is primarily governed by impact deformations and ploughing effect (Bhushan, 1999b; Tambe and Bhushan, 2005b). Thus, while low E materials are able to absorb most of the impacts during sliding, for the high E materials, the impacts during sliding result in high friction. DLC is the only high E material which shows a decrease in coefficient of friction at very high sliding velocities. The reason for this anomaly is the phase transformation of the amorphous DLC to a low shear strength graphite like phase (Voevodin et al., 1996; Grill, 1997; Tambe and Bhushan, 2005e). The sharp Si$_3$N$_4$ tip used in AFM studies (30-50 nm radius) gives rise
Figure 6.4: Velocity dependence of adhesive force and coefficient of friction for various materials and contour plots giving the dependence as a function of Young’s modulus

(Tambe and Bhushan, 2005f)
to contact pressures in the range of 1.8-3.8 GPa for DLC films corresponding to normal loads of 10-100 nN (assuming Hertzian contact analysis for elastic single asperity contact) and Voevodin et al. (1996) have reported formation of debris with polycrystalline graphite like structure for contact pressures in the range of 0.8-1.1 GPa.

The contour map reveals a small central zone of very low friction. The corresponding adhesive force values for this zone are also moderate. This can be considered as a ‘sweet spot’ and corresponds to an ideal material that a tribologist would like to choose. HOPG falls in this zone. Various other zones of interest are summarized in Fig. 6.5. They indicate the dependence of Young’s modulus on the operating parameters and thus can be used as a guide for material selection for various nanotechnology applications. We find that, from the tribology point of view, low E materials show promise for high sliding velocity applications, while high E materials are more suitable for relatively lower sliding velocities.
Figure 6.5: Map for identifying materials with low friction and adhesion. At low velocities (<10 μm/s), the coefficient of friction (μ) decreases logarithmically with Young’s modulus. At high velocities (>1 m/s), μ increases with an increase in the Young’s modulus. The ‘sweet spot’ corresponds to materials with low μ and moderate adhesion. The ideal zone for material selection is however the one where both μ and adhesion are either low or moderate and is the shaded diagonal portion (Tambe and Bhushan, 2005f)
6.3 DLC as a protective coating for nanotechnology applications

Many MEMS/NEMS applications have already reached the commercial market. Air bag deployment sensors used in automobiles, DMDs used for digital light processing projection displays in and RF switches are examples of such devices (Bhushan, 2004). Inspite of their popularity though, many nanotechnology applications remain dogged by severe drawbacks due to some common potential failure mechanisms. In order to increase reliability of these devices various tribological issues such as friction, adhesion and wear and their occurrence as a result of mechanical deficiencies arising from fatigue and fracture need to be addressed (Arney, 2001; Bhushan, 1998, 1999a, 2004; Boer and Mayer, 2001; Man, 2001; Man et al., 1998; Tanner et al., 1999). For example stringent lifetime requirements of the DMDs demand micromirror switching cycles to be close to 2.5 trillion (Liu and Bhushan, 2004). Micromirror hinge mechanism fatigue is therefore an important issue and can critically influence DMD reliability (Hornbeck, 2001; Douglass, 2003). High stress cycle fatigue induced failure of silicon based microfilms has been reported to lead to subsequent wear and eventual cracking of the surface layers (Muhlstein et al., 2001).

DLC is considered a strong candidate as a protective coating for MEMS/NEMS applications owing to its unique combination of desirable properties including low coefficients of friction, high hardness and wear resistance and chemical inertness to both acids and alkalis (Grill, 1997; Bhushan, 1999c; Bhushan et al., 2004). DLC is already very widely used in the magnetic data storage industry for coating magnetic tapes and hard disks (Bhushan, 2000). Various researchers have investigated the nanoscale tribological and mechanical properties of DLC coatings (Bhushan and Koinkar, 1995;
These studies indicate that the nanowear and film cracking behavior is strongly affected by variations in the film thickness, the applied normal load, the number of sliding cycles, the deposition technique used for the DLC films and the magnitude of stress and its amplitude that can ultimately result in fatigue induced cracking of the coating.

One example where DLC has been proven to resist cracking and wear is magnetic tapes (Bhushan, 2000). In magnetic tape drives, the tapes are subjected to dynamic loading when they are wound and unwound over reels and as they pass over the guides and the magnetic head. Apart from this, the tapes are subject to much higher dynamic stresses than the normal operating axial tension during start-stops, instantaneous speed variations and tape vibrations (Bhushan, 2000). This leads to cracking in the magnetic coating and affects tape reliability. Tambe and Bhushan (2004b) developed an AFM based technique for in-situ characterization of thin films under monotonic and dynamic loading. They studied magnetic tapes with and without DLC coatings and compared the crack growth mechanisms. They found that the DLC coating significantly increased the resistance to crack formation. Figure 6.6 shows the increase in crack depth with tensile strain for a metal evaporated (ME) magnetic tape. Also shown are 2D cross sectional profiles of the crack measured using an AFM at different stages of crack growth and a schematic illustration of cracking of the DLC coating and the subsequent delamination and bulging of the coating.

The significant interest in DLC for tribological applications arises from the low friction and the ultra low wear of DLC films. This has been attributed to formation of a
Figure 6.6: Stages in crack growth in a metal evaporated (ME) tape with DLC coating, 2D cross sectional AFM images and crack propagation mechanism showing: Stage I – Crack initiation, Stage II – Delamination and subsequent bulging as crack reaches interface of the DLC and magnetic coatings, and Stage III – Crack penetrates through the magnetic coating (Tambe and Bhushan, 2004a)
low shear strength graphite-like layer at the sliding interface as a result of thermal and strain effects generated during sliding. This transfer layer is believed to be formed by a friction induced transformation of the top layer of the DLC film (Erdemir et al., 1995, 1996; Voevodin et al., 1996) and its shear strength and its adhesion to the sliding surfaces is known to be affected by the environment and by the normal load and sliding velocity (Grill, 1997).

Tambe and Bhushan (2005e) investigated the phase transformation of DLC on the nanoscale by studying friction, adhesion, durability and wear of the DLC coating. Figure 6.7 gives a contour map for friction force as a function of sliding velocity and the normal load. The contour lines, representing constant friction force, were found to be concentric. This indicates that at relatively high normal loads and sliding velocities the contour map would reach a peak point and this would correspond to the highest friction force. Beyond that point, any further increase in the normal load or the sliding velocity will result in a decrease in the friction force. Such a decrease implies a phase transformation whereby a low shear strength layer is formed at the sliding interface. To explore this possibility, the velocity dependence of friction force was studied at a constant normal load of 70 nN. The adhesive force was also measured as a function of the sliding velocity.

Figure 6.8 gives the velocity dependence of the friction force and the adhesive force over a range of sliding velocities. The friction force showed an initial logarithmic increase with velocity followed by a near logarithmic decrease beyond a certain critical velocity. The initial increase in friction force is known to be a result of atomic scale stick slip (Riedo et al., 2003; Tambe and Bhushan, 2005b) and previous researchers have predicted that the increase in friction force would proceed until a critical velocity of 400
Figure 6.7: Friction contour map showing constant friction force lines (in nN) as a function of the normal load and the sliding velocity (Tambe and Bhushan, 2005e)
Figure 6.8: Velocity dependence of friction and adhesion for DLC films at a constant normal load of 70 nN. Inset: velocity dependence of HOPG at 70 nN normal load. Static adhesive force measurements are also indicated for comparison (Tambe and Bhushan, 2005e)
µm/s (Riedo et al., 2002). Our experiments indicate that the critical velocity at which the friction behavior reverses is very close to 400 µm/s. Interestingly, beyond the critical velocity the friction force drops nearly logarithmically with any further increase in the velocity. The adhesive force measurements seem to follow the trends in the friction force very closely. Initially the adhesive force remained constant but beyond the critical velocity there was an increase in the adhesive force with an increase in the sliding velocity. The decrease in friction force beyond a critical velocity is believed to be the result of phase transformation of DLC to a low shear strength graphite-like phase by a sp³ to sp² phase transition.

Voevodin et al. (1996) have reported formation of debris with polycrystalline graphite like structure for contact pressures in the range of 0.8-1.1 GPa and sliding velocities of 0.2 m/s for their experiments on the macroscale. We can determine the contact pressure for our nanoscale experiments based on single asperity Hertzian contact analysis. For the sharp Si₃N₄ tip (Young’s modulus, E=310 GPa; poisson’s ratio, v=0.22 (Bhushan and Gupta, 1997)) sliding on the DLC surface (E=280 GPa, v=0.25 (Bhushan, 1999c)), the resulting contact pressures are in the range of 1.8-3.8 GPa corresponding to normal loads of 10-100 nN (Tambe and Bhushan, 2005e). In the experiments the sliding velocities were much lower than those used by Voevodin et al. (1996). However, contacts between real engineering surfaces are multiasperity contacts, even on the nanoscale. Thus the actual contact pressures at the sliding interface are much higher than the ones calculated above. The higher contact pressures on the nanoscales combined with the frictional energy dissipation due to asperity impacts will accelerate the phase transformation process.
To verify the phase transformation of DLC films, experiments were run on highly oriented pyrolytic graphite (HOPG). The velocity dependence of friction force for HOPG is shown in Fig. 6.8 (inset). For HOPG, the friction force initially increased with velocity but then leveled off beyond a certain critical velocity. The friction force values for DLC and HOPG at the highest velocity of 10 mm/s were found to be nearly the same. Also, the adhesive force measurements performed on HOPG under identical environmental conditions gave a value of about 50-60 nN which is close to the adhesive force obtained for DLC at the highest sliding velocity of 10 mm/s. These findings suggest that there could be some friction induced phase transformation of the DLC sample surface leading to the formation of a low shear strength graphite-like layer.

Next the effect of continuous sliding on the sliding interface was studied. Experiments were performed at a normal load of 150 nN and at two sliding velocities: 250 µm/s and 10 mm/s. Figure 6.9 gives the friction force as a function of the sliding distance. The friction force was found to increase with sliding distance for the durability test at 250 µm/s, however, it decreased with sliding distance for the durability test at 10 mm/s. The reduction in the friction force in long duration tests has been attributed to the formation of a low shear strength layer at the sliding interface by previous researchers (Voevodin et al., 1996; Grill, 1997). Repeated friction is believed to raise the interface temperature to a point where there is a sp³ to sp² phase transition of some DLC into a graphite-like phase. It is believed that at the lower sliding velocity the low shear strength transfer layer is not formed at the sliding interface, however, the higher energy dissipation resulting from asperity impacts at the high velocity probably causes a sp³ to sp² phase transition, resulting in a drop in friction force with sliding distance. Miyoshi (1990) has reported
that the formation of a transfer layer requires a certain total amount of friction energy and this has been supported by other studies (Erdemir et al., 1995).

In their studies, Voevodin et al. (1996) have suggested a mechanism for the phase transition process and the subsequent accumulation of disordered sp² carbon transfer layer at the sliding interface. To further investigate similar phase transformation on the nanoscales, wear maps were created on the DLC sample by running novel experiments and then imaging the wear area. The AFM tip was slid perpendicular to the direction of motion of the sample through controlled tip movements and by ramping up the normal load gradually during its travel or by varying the rate of AFM tip movement for studying the surface wear. Figure 4.9 gives the results obtained from the wear tests. The wear mark
generated suggests that the effect of sliding velocity is more profound than that of the normal load. The wear maps indicate that wear debris particles are generated only for certain combinations of sliding velocities, normal loads and number of sliding cycles.

The presence of wear particles and the corresponding low friction force and high adhesive force values at high sliding velocities (Figs. 4.9, 4.10, 6.8 and 6.9) are all indicative of a phase transformation by a mechanism similar to that reported on the macro- and microscales for DLC (Voevodin et al., 1996; Grill, 1997).

In conclusion, DLC films, because of their low coefficients of friction, high hardness and wear resistance, have significant importance for tribological applications and are potential protective coatings for nanotechnology applications.
APPENDIX A

METHODS FOR CONDUCTING MICRO/NANOSCALE STUDIES

Micro/nanoscale investigations are performed in a variety of ways including techniques such as scanning electron microscopy (SEM), x-ray spectroscopy (XPS), Auger electron spectroscopy (AES), transmission electron microscopy (TEM), infrared spectroscopy (FTIR), Raman spectroscopy and atomic force microscopy (AFM) and its various sister techniques such as magnetic force microscopy (MFM), scanning tunneling microscopy (STM), scanning capacitance microscopy, torsional resonance mode AFM (TR-AFM) and acoustic friction force microscopy (AFAM). Based on the analysis depths and the resolution and detection limits these techniques are suitable for certain studies and not for others. Figure A.1 shows the typical analysis depths for various techniques and Fig. A.2 shows the analytical resolution vs. the detection limit for these techniques. Each technique has its unique advantages and disadvantages.
Figure A.1: Technical analysis depths for various techniques for conducting micro/nanoscale investigations (source: American Vacuum Society 2003 International Symposium handout)
Figure A.2: Analytical resolution and detection limits for various techniques for conducting micro/nanoscale investigations (source: American Vacuum Society 2003 International Symposium handout.)
APPENDIX B

HIGH VELOCITY STAGE MOUNTING PLATE

The high velocity stage used for the experiments was mounted on the AFM motorized stage using an aluminum mounting plate (Fig. B.1). The aluminum mounting plate was designed to have provision for clamping to the AFM motorized stage and that allowed to locate the piezo stage below the AFM cantilever using the AFM controller. To reduce vibrations, originating from high frequency operation of the piezo stage, damping tape was used between the aluminum plate and the piezo stage. The stage was located so as to allow appropriate distances on either side for ease of access during sample mounting.

The samples themselves were mounted on a specially machined clamping sheet (Fig. B.2). The clamping sheet was a thin PVC sheet designed with a weight criteria in mind. The piezo stage operation can be hampered by large loads. To minimize this possibility and also to allow for stage damage from frequent sample mounting, a PVC plate was selected. The piezo stage calibrations as detailed in chapter 2 were conducted with the PVC plate on.
Figure B.1: Aluminum mounting plate for the high velocity stage.
Figure B.2: Sample clamping plate. The plate is mounted on the high velocity stage and is made of a thin PVC sheet.
APPENDIX C

EXPERIMENT DESIGN AND DATA COLLECTION

During data collection the capacitive feedback loop maintains a constant velocity profile over the entire scan length for the piezo stage. This ensures that the friction data obtained using the modified setup is the correct estimate of the friction resulting from the relative sliding between the tip and the sample even at high velocities. To eliminate any further discrepancies in the friction measurements that could result from any uncharacteristic behavior of the piezo stage during reversals, only the central portion of the TMR signals are considered while calculating the average values of friction (see Fig. C.1)
Figure C.1: Friction data averaging using only central half portion of the TMR signals for discounting any unforeseen inconsistencies arising from piezo stage reversals, particularly at high velocities.
Further the measurements obtained using the high sliding velocity piezo stage were optimized by monitoring the reproducibility of the data as well as by changing data collection parameters. The two most important parameters for any friction measurement are the sampling interval and the sampling rate.

The sampling rate is the number of data points collected per sec. As the scanning frequency (velocity of the stage) is increased the number of points collected per cycle automatically goes down and it is necessary that sufficient number of data points are collected per cycle at high velocities to avoid any inconsistencies in the measured friction values. Figure C.2 shows the effect of change in sampling rate on the measured friction values. The data shown in Fig. C.2 corresponds to one cycle of forward and reverse traces by the AFM cantilever on the sample surface (this is similar to the TMR signal referred in previous section). The data is collected at a scan frequency of 20 Hz and at various sampling rates. The effect of sampling rate is evident from the Fig. C.2. Many experiments discussed in this dissertation in later chapters have been conducted at high scanning frequencies (up to 250 Hz). To avoid any aliasing effects in friction measurements the sampling interval was chosen to be 10,000 points/s for scan frequencies up to 50 Hz. For scan frequencies greater than 50 Hz, the sampling rate was set to 20,000 points/s.

The sampling interval is the number of data points that are collected per µm of the scan length. If the sampling interval is very large in comparison to the total scan length then it can lead to effects similar to aliasing effects and result in a lot of information being lost or overlooked. In all the experiments reported in this dissertation the scan sizes selected from 2 to 25 µm. The friction force measurements are plotted as a function of the
Figure C.2: Effect of sampling rate on friction force measurement
sampling interval in Fig. C.3 for three different scan sizes. A large effect is seen in the measured friction force values at low sampling interval. This effect becomes more pronounced, as expected, for larger scan sizes. However, as the sampling interval is increased to higher values the measured values of friction force stabilize. This indicates that for higher sampling intervals the friction force is no more affected by the number of data points being collected per µm of the scan length. For all experiments reported in this dissertation the sampling interval was set to at least 100 points/µm. It should be noted that the sampling interval can be changed by changing the scan frequency and the sampling rate.

For all the friction and adhesive force measurements reported in this dissertation the values were always within ± 5 % and never more than ± 10 % in some cases like those at high velocities, unless otherwise stated. More details regarding the specific measurements of adhesive force and friction force values amongst other measurements are discussed throughout the dissertation wherever pertinent.
Figure C.3: Effect of sampling interval on friction force measurement
APPENDIX D

FRICION FORCE “CONVERSION FACTOR” AND TIP RADIUS CALIBRATIONS

D.1 Cantilever ‘conversion factor’ calibrations

Friction force measurements in AFM studies are based on the torsional deflections of the cantilever resulting from relative sliding between the AFM tip and the sample. The cantilever deflections are monitored from the laser deflection and the “SUM” signals on the AFM photodiode. The friction force can be calculated by converting the voltage measurements of the photodiode into Newton units. All the AFM cantilevers used in this research were calibrated to calculate friction force in Newton units. The standard Method 1 – Method 2 approach developed by Ruan and Bhushan (1994) was used for performing these calibrations.

To describe the calibration process in brief, the cantilever is first scanned on the sample surface at 0° scan angle. This corresponds to the cantilever motion along the long axis. The deflections of the cantilever are monitored for change in normal load (marked by change in piezo center position) and a plot of the deflection vs. piezo center position is made to get the coefficient of friction. Then the cantilever is scanned at 90° scan angle. This corresponds to cantilever motion along the lateral direction (perpendicular to the
long axis). Once again the cantilever deflections (TMR signals) are monitored as a function of normal load. The plot of TMR vs. normal load then gives the coefficient of friction again but in V/N units. Since the coefficient of friction between two materials will remain same irrespective of the direction of sliding, the conversion factor (V to N) can be calculated using data obtained during the 0° (Method 1) and 90° (Method 2) scan directions.

All tips were calibrated in this fashion and the data is presented next:

- **Short wide Si₃N₄** tips with nominal spring constant (cantilever stiffness) of 0.58 N/m
  
  **Method 1:** (5 such tests were performed, only one plot is shown here)

  ![Method 1 Graph](image1)

  

  Method 2: (5 such tests were performed, only one plot is shown here)

  ![Method 2 Graph](image2)
Calibration factor by equating slopes is 53 nN/V and the corresponding plot is as below:

- Short thin Si$_3$N$_4$ tips with nominal spring constant (cantilever stiffness) of 0.32 N/m

Method 2:

```
y = 1.2729x + 42.95
R^2 = 0.9935
```

Calibration factor by equating slopes is 40 nN/V

- Long wide Si$_3$N$_4$ tips with nominal spring constant (cantilever stiffness) of 0.12 N/m

Method 2:
Calibration factor by equating slopes is 20 nN/V

- *Si tips (Ti/Pt coated)* with nominal spring constant (cantilever stiffness) of 3.5 N/m
  
  (These tips were used for the wear tests)

Method 2:

Calibration factor by equating slopes is 0.5047 nN/mV and the corresponding plot is as below:
- **Diamond tips** with nominal spring constant (cantilever stiffness) of 10 N/m (These tips were used for the durability tests)

Method 2: (multiple tests are shown in figure)

Calibration factor by equating slopes is 0.1667 μN/mV
D.2 AFM tip radius calibration using calibration grating

For the durability tests, the AFM tip radius was measured before and after the tests. The wear of the AFM tip is an indication of how the sample surface wear outs. For most of the experiments the tips used were harder than the sample surface and not much wear was expected on the tip itself, however it was found that in general after the wear tests on Si (100) and DLC samples the AFM tip radius had slightly increased.

The determination of the AFM tip is based on a “blind reconstruction process”. In this method the AFM tip is scanned on a calibration grating with sharp features of known dimensions. The AFM scanned image is a dilation of the real specimen surface and the reflection of the probe tip surface. If the real surface is known, then the tip surface can be obtained by “deconvolution” of the obtained image and the real specimen surface. Ideally, to get a desirable estimation of the tip shape, the specimen should contain sharp features and high relief. An analytical algorithm can then be utilized to deconvolute the data to mathematically calculate the tip radius.

For the purpose of this dissertation the tip shape was characterized by "blind tip reconstruction" using commercially available software Scanning Probe Image Processor (SPIP, Image Metrology A/S, Denmark). A grating with known surface features that are conical pyramids with peak radius of <10 nm (TGT1, NT-MDT, www.ntmdt.ru Zelenograd, Moscow, Russia) was used for characterization (see Fig. D1).
Figure D.1: TGT1 grating schematic and SEM image showing conical pyramidal features with peak radius $<$10 nm
APPENDIX E

SAMPLE CLEANING AND PREPARATION PROCEDURES

E.1 Sample cleaning

Samples used for during the research were cleaned before making friction and adhesion measurements. Si (100), DLC and PDMS were ultrasonically cleaned in acetone bath while PMMA was ultrasonically cleaned in isopropyl alcohol bath. Z-15 and Z-DOL samples were prepared by directly depositing on Si (100) wafers that were ultrasonically cleaned in acetone bath. Further details can be found in Liu and Bhushan (2003b).

E.2 Z-15 and Z-DOL sample preparation procedure

The Z-15 samples for the research were prepared using the step-by-step procedure as outlined below:

1. Take a silicon wafer sample
2. Clean thoroughly in acetone for 10 mins in ultrasonic bath
3. Remove sample and let it dry for a while, 2-3 mins. Keep this beaker separate
4. Take FC-72 solution in the Z-15 beaker,
5. dip cleaned Si sample in the beaker and place for about 7 mins
6. remove sample from the beaker and clip it to the motorized stage

7. put FC-72 solution from the beaker into the “used FC-72” jar

8. in the same beaker now take Z-15, ensure that the solution you have taken is enough
   for the sample to dip in it. Take this Z-15 from the bottle saying 0.1% (1 ml Z-15 in
   500 ml HT70) (Jan 02). This solution is actually 0.2 % strong.

9. place this beaker below the clip on the motorized stage

10. select slowest speed for the stage using speed knob lo and select 30 on the dial knob

11. forward movement corresponds to upward movement and backward is downwards

12. dip clipped sample in Z-15 beaker and place for 10 mins

13. start the motorized stage, slowest speed, forward direction and allow the sample to
   completely clear the beaker. Slower the speed thinner the film coated. This speed
   setting will give an approx film thickness of 2-3 nm

14. pour Z-15 from the beaker back into the bottle saying 0.1 % Z-15

15. use ellipsometer to measure the actual thickness of film deposited, you will need
   another clean silicon sample from same batch to act as reference reading for the
   ellipsometer.

   For Z-DOL preparation the bonded films were baked at 150 °C for 30 mins and then
   washed in FC-72 solution to wash off any fraction of unbonded molecules.

   Further details regarding the procedure for lubricant film preparation can be found in
   Liu and Bhushan (2003b).
APPENDIX F

SOFTWARE CODE FOR DATA PROCESSING AND MACROS FOR
CONTROLLED MOVEMENT OF AFM TIP

For all the experiments performed during this research using the high velocity
stage and the microtriboapparatus, the raw friction signals corresponding to the lateral
deflection of the AFM cantilever (or the stainless steel cantilever as for the
microtriboapparatus) were collected using Snap Master™ Version 3.5 (HEM Data
Corporation, MI). For data processing the raw data files were processed using MATLAB
subroutines/programs. The algorithms used for the friction data processing are included
in this appendix. Apart from friction data processing, programs were also written to plot
contour maps. Friction force was plotted as a function of normal load and sliding velocity
as well as a function of Young’s modulus of the material and sliding velocity.
Documentation provided in each of the programs sufficiently describes the algorithms
and the logic involved.
F.1 Friction force data processing

F.1.1 Friction processing from raw AFM cantilever lateral deflection signals

% Program by: Nikhil S. Tambe (tambe.2@osu.edu)
% ----------------------------------------------------------------------
% Program to calculate TMR (friction) signal from raw data file
% Input is Snap master data file *.csv
% Output is TMR value averaged for all given data and in Volts
% ----------------------------------------------------------------------
% Version 1.6.2 Modified 03/20/2004. Added small routine to save one cycle
% TMR data in ascii format to plot it in Excel.
% Added subroutine to plot PZT input voltage and friction
% profiles in Excel by saving data in ascii
% Version 1.6.1 Modified 03/04/2004. Made TMR plotting permanent by dividing
% plot area into third part. TMR value is also plotted on
% graph now. Changed order so that TMR is at the top..
% Version 1.6.0 Debugged TMR subroutine
% Debugged problem with data calculations at 100 Hz scan
% frequencies and above. Check documentation at end.
% Version 1.5.0 02/11/2004 Added subroutine to plot one TMR cycle. Removed
% unnecessary documentation and unused (alternative) code lines
% Version 1.4.1 Modified 01/16/2004 Fixed bug in plotting low frequency data, if loop
% Version 1.4.0 Modified 10/07/2003 changed way files are read, now using 'csvread'
% instead of 'load'; because of this program wont require any
% preprocessing of files to remove channel number
% Version 1.3.1 Modified 10/02/2003 plot all data on one graph, used 'subplot'
% Version 1.3.0 Modified 09/26/2003 temporarily set variables F,t & plotdata
% to their std. values to avoid inputting values each time
% Version 1.2.1 Modified 09/15/2003 created variables 'avg1' and 'avg2', now
% can average between any two given points in the data
% Version 1.2.0 Modified 09/04/2003 added variable 'avg'
% Version 1.1.0 Modified 08/05/2003
% Version 1.0.0 Created on 07/25/2003
% ----------------------------------------------------------------------

% Run from command line in MATLAB. Call to afmpzt function executes the
% code. Reference variables need to be in correct order!
% function afmpzt(filename, sampling rate, scanning frequency, number of frames,
% time for each frame in seconds, avg-number of data points to consider for averaging
% plotdata, plotprofile (voltage and friction) --> 0=no, 1=yes, 2=plot and save

function afmpzt(filename,s,f,t,plotdata,plotprofile,buffer)
F=3; avg1=0; avg2=50; % Default values
% Load the raw datafile into Matlab.
% M = csvread('filename',row,col,range) is the syntax for this command and
% row and column numbers are zero based, i.e. row one is numbered zero
% AA(1:(s*F*t))=csvread(filename,1,0,[1,0,(s*F*t),0]);

% Determination of TMR by averaging and calculating T(race) and R(etrace) signals
start=(s/(2*f)-mod((s/(2*f)),4))/4;
if ((F-1)*f*t)<avg2
    max=((F-1)*f*t); % For low scan frequency consider all available cycles
    min=avg1;
else max=avg2;  % For high scan frequency consider only first 'avg' number of cycles
    min=avg1;
end

% ************** Feb 11, 2004 **************
% Discovered a bug in the way data is processed for high frequencies
% (100 Hz and above). Check end of program for complete documentation of this error.
% Program is modified by adding a 'buffer' to 'dataseed'.

if buffer==-1 % set for data collection rate of 10,000 only. Any other rate and buffer
    value will need to be changed...
    if f==1
        buffer=400;
    elseif f==5    buffer=80;
    elseif f==10   buffer=40;
    elseif f==20   buffer=30;
    elseif f==50   buffer=55;
    elseif f==100  buffer=70;
    elseif f==250  buffer=5;
    else buffer=0;
    end
end

for cycle=min:1:max-1
    dataseed=s*t+buffer+cycle*s/f; %reject first frame data and count points per cycle
    % Only central half portions of TMR are considered, rest data is neglected,
    % this particularly removes any 'change of direction' related noise in data.
    begin1=dataseed+start;   end1=dataseed+3*start;
    begin2=dataseed+5*start;   end2=dataseed+7*start;
    T(cycle-min+1)=mean(AA(begin1:end1)); % calculates mean of values stored in AT
    R(cycle-min+1)=mean(AA(begin2:end2)); % calculates mean of values stored in AR
end

TMR=abs(mean(T)-mean(R)) % Required TMR value
% Visual check. Plots data input and output to check for accuracy.
if plotdata>0
subplot(3,1,2); plot(1:(s*F*t), AA(1:(s*F*t)))
subplot(3,1,3); plot(min:max-1, T(1:max-min), min:max-1, R(1:max-min))

% BB is the matrix to hold friction data for one cycle
BB(1:(s/f))=AA((s*t+buffer+1):((s*t+buffer+1)+s/f-1)); % first cycle data after
rejecting first frame

token=str2num(strtok(filename,'-')); % above command decodes the filename to get 'scan size' and then converts
% data type to get numeric value
% CC is the dummy matrix to hold the actual scan size and mirror data
CC(1:s/f)=(1:s/f).*(token/(s/(2*f)));
CC((s/(2*f)+1):s/f)=CC(s/f+1-((s/(2*f)+1):s/f));
subplot(3,1,1); plot(CC, BB); xlabel('Scan size (um)'); ylabel('TMR (V)'); title(TMR)
% save TMR data for Excel plotting or similar
if plotdata==2
    TempName1=[strtok(filename,'.'), 'TMR'];
    BB=BB'; CC=CC'; save(TempName1, 'BB', 'CC', '-ascii')
end
end

if plotprofile>0
    % Subroutine to plot PZT input voltage and friction signals as a function
    % of time
    % Load the raw data to PZT stage input voltage values
    VV(1:(s*F*t))=csvread(filename,1,1,[1,1,(s*F*t),1]);
    % Plot data for 5 cycles starting from the second frame of data collection
    VV1=VV(s*t:(s*t+5*s/f));
    AA1=AA(s*t:(s*t+5*s/f));
    TT1=0:(1/s):5/f;
    figure; subplot(2,1,1); plot(TT1, VV1); subplot(2,1,2); plot(TT1, AA1);
    if plotprofile==2
        TempName2=[strtok(filename,'.'), 'profiles'];
        TT1=TT1'; VV1=VV1'; AA1=AA1';
        save(TempName2,'TT1','VV1','AA1', '-ascii')
    end
end

% ************** Feb 11, 2004 ***************
% Discovered a bug in the way data is processed for high frequencies
% (100 Hz and above). Program is modified by adding a 'buffer' to 'dataseed'.
% Error is generated from the way that data is collected. I use a trigger
% signal corresponding to the PZT input voltage to start data collection.
% The trigger is set so as to start whenever a positive rising slope is
% recorded for the triangular voltage input pulse between 0 and 0.01 V. At
% low frequencies the amount of data being neglected is very less to cause
% mathematical havoc but the problem becomes significant when frequencies
% are above 100 Hz. Below table highlights this problem....
%
% at 100 Hz one cycle is completed in 10 ms (rise to VPP is in 5 ms):
% scan size VPP 0.01 V rise time max datapts lost at 10000 per sec
% 2 um 0.3 V 0.1667 ms 1667
% 5 um 0.78 V 0.0641 ms 641
% 10 um 1.6 V 0.0313 ms 313
% 25 um 4 V 0.0125 ms 125
%
% After checking various profiles buffer=10 is best suited for 100 Hz and
% hence is selected while modifying the program

F.1.2 Friction processing signal for microtriboapparatus

% Program by: Nikhil S. Tambe (tambe.2@osu.edu)
% --------------------------------------------------------------
% Program to calculate TMR (friction) signal from raw data file
% Output is TMR value averaged for all given data and in Volts
% --------------------------------------------------------------
% Version 1.1 Modified 5/1/2004 Previously criteria for trace or
% retrace value was considered as values above and below zero.
% Found this to be untrue for all cases and hence modified by
% instead saving alternate values in R and T matrices.
% --------------------------------------------------------------

function tribo(filename)
A=load(filename);
length=size(A);
s=length(1,1); % total number of data points
%A load data in proper format
for i=1:s
    if A(i,7)<0
        sgn=-1;
    else sgn=1;
    end
    B(i,1)=sgn*(abs(A(i,7))*1e6+A(i,8));
end
B(:,2)=A(:,11);
%check data by plotting
plot(B(:,2),B(:,1))

%calculate TMR
j=1;k=1;
% j and k are dummy variables corresponding to # of points
taken while averaging friction values
count=1; flag=0;
% count is the number of cycles. I always use 5 cycles.
% Flag value indicates whether its a trace or retrace cycle
for i=1:s-1
  if B(i,2)>1750 & B(i,2)<2500
    if flag==0
      R(j)=B(i,1);
      j=j+1;
    else
      T(k)=B(i,1);
      k=k+1;
    end
  end
  if B(i,2)>B(i+1,2)
    flag=1;
  else
    flag=0;
  end
end
% visual check
%figure;plot(1:j-1,R(1:j-1),1:k-1,T(1:k-1))
TMR=abs(mean(T)-mean(R))
%FricForce=(TMR/2)*309*1e-6

F.1.3 Contour plotting: Friction as a function of normal load and sliding velocity

% Program by: Nikhil S. Tambe (tambe.2@osu.edu)
% ---------------------------------------------------------------------------
% Version 1.1.0 Modified 20 Mar 2004.
% Version 1.0.0 First created 7 Feb 2004
% ---------------------------------------------------------------------------
% Program to plot contour showing influence of velocity and normal load on
% friction force
% ---------------------------------------------------------------------------
function FrictionMap(filename,levels,s)
A=load(filename); % temp filename where the data is stored
i=size(A);
[C h]=contour(A(1,2:i),A(2:i,1),A(2:i,2:i),levels,'-k');
% contour(X=velocity, Y=normal load, Z=friction force)
set(gca,'XScale','log');xlabel('Velocity (um/s)');ylabel('Normal load (nN)');
Title(['Friction map for ', strtok(filename,'.')])
clabel(C,'manual');% manual allows labelling contours manually
if s==1
saveas(gcf,strtok(filename,'.'),'tif')
end

F.1.4 Contour plotting: Friction as a function of sliding velocity and Young’s modulus

% Program by: Nikhil S. Tambe (tambe.2@osu.edu)
% % Version 1.2.0 Modified 17 Jul 2004
% % For plotting Young's modulus as a function of velocity
% % Version 1.1.0 Modified 20 Mar 2004.
% % Version 1.0.0 First created 7 Feb 2004
% % %
% % Program to plot contour showing influence of velocity and normal load on friction force
% % %
function ModulusContourMap(filename,levels,s)
A=load(filename); % temp filename where the data is stored
i=size(A);
[C h]=contourf(A(1,2:i(2)),A(2:i(1),1),A(2:i(1),2:i(2)),levels,'-k');
% contour(X=velocity, Y=normal load, Z=friction force)
set(gca,'XScale','log','YScale','log');xlabel('Youngs modulus (GPa)');ylabel('Velocity (um/s)');
Title(['Contour map ', strtok(filename,'.'))]
clabel(C,'manual');% manual allows labelling contours manually
if s==1
saveas(gcf,strtok(filename,'.'),'tif')
end

end
F.2 Macros for controlled movement of AFM tip: Nanowear mapping

Nanowear mapping experiments performed using the AFM required the movement of the AFM tip in customized ways very different from the normal raster scanning operation. This requirement was met by using the lithography module of the Nanoscope controller. This module allows the user to write macros (programs) that direct the controller to perform controlled movements of the piezo. This programming interface called NanoScript™, is based on the ‘C’ programming language and uses similar syntax. This appendix contains macros written for the nanowear mapping experiments performed in this research. More details on the commands and other information on the Lithography module and NanoScript can be found in the Nanoscope® Command Reference Manual for Version 4.42, Appendix D: Lithography from Digital Instruments.
F.2.1 Scratch.m program: Effect of normal load at constant sliding velocity and number of sliding cycles

// scratch.m
// Scratch test for AFM Program
// Modified on 27 Jul 2004 by Nikhil S. Tambe
#include <litho.h>
void main()
{
    LITHO_BEGIN
    LithoDisplayStatusBox();  // display litho status box
    LithoScan(FALSE);         // turn off scanning
    LithoCenterXY();          // move tip to center of field
    // Parameters
    double scr_lngth=5.0;     // Scratch length in microns
    int incr=100;              // Normal load increment steps
    double rate=.5;           // Tip speed in microns/second
    double iload=-1.778;      // Magnitude of initial normal load voltage
    double fload=1.786;       // Magnitude of final normal load voltage
    double dir=1.0;           // Scratch direction, positive (1) or negative (-1)
    double dstep=dir*(scr_lngth/incr); // Length of segment for each normal load increment
    double fstep=(fload-iload)/incr; // Magnitude of normal load increment in volt
    int i;
    // Commands start here
    LithoPause(10);            // Time in seconds for which the AFM will pause.
    //LithoTranslate(0,-5,rate)  // Move tip 5 micron to left before starting scratch test
    for(i=1;i<=incr;i++)
    {
        setvolt=iload+fstep*i;
        LithoSet(lsSetpoint,setvolt);
        LithoTranslate(0, dstep, rate);
    }
    LithoSet(lsSetpoint,iload);
    LithoPause(10);
    LITHO_END
}
F.2.2 Scratch-.m program: Effect of number of sliding cycles at constant sliding velocity and normal load

// scratch-.m
// Scratch test for AFM Program: Velocity vs number of cycles
// Modified on 31 Jul 2004 by Nikhil S. Tambe
#include <litho.h>
void main()
{
    LITHO_BEGIN
    LithoDisplayStatusBox(); // display litho status box
    LithoScan(FALSE);        // turn off scanning
    LithoCenterXY();         // move tip to center of field
    // Parameters
    double scr_lngth=5.0;    // Scratch length in microns
    int incr=100;            // Normal load increment steps
    double rate=5;           // Tip speed in microns/second
    double iload=-1.778;     // Magnitude of normal load voltage
    double dir=1.0;          // Scratch direction, positive (1) or negative (-1)
    double dstep=dir*(scr_lngth/incr); // Length of segment for each normal load increment
    double rstep=rate/incr;  // Magnitude of increment for translation rate
    int i;
    // Commands start here
    LithoPause(10);          // Time in seconds for which the AFM will pause.
    LithoSet(lsSetpoint,iload); // Set normal load

    for(i=1;i<=incr;i++)
    {
        LithoTranslate(0, dstep, rate);
        rate=rate-rstep;
    }
    LithoPause(10);
    LITHO_END
}

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F.2.3 Scratchv.m program: Effect of sliding velocity at constant number of sliding cycles and normal load

// scratch.m  
// Scratch test for AFM Program  
// Program to study effect of velocity by keeping normal load and number of sliding cycles constant  
// Modified on 2 Aug 2004 by Nikhil S. Tambe  
#include <litho.h>  
void main()  
{  
    LITHO_BEGIN  
    LithoDisplayStatusBox(); // display litho status box  
    LithoScan(FALSE); // turn off scanning  
    LithoCenterXY(); // move tip to center of field  

    // Parameters  
    double scr_lngth=5.0; // Scratch length in microns  
    int incr=4; // Velocity increments  
    double iload=-1.778; // Magnitude of initial normal load voltage  
    double fload=1.786; // Magnitude of final normal load voltage  
    double dir=1.0; // Scratch direction, positive (1) or negative (-1)  
    double dstep=dir*(scr_lngth/incr); // Length of segment for each normal load increment  
    int i;  
    // Commands start here  
    LithoSet(lsSetpoint,fload); // Set normal load  
    LithoPause(10); // Time in seconds for which the AFM will pause.  
    LithoTranslate(0, dstep, 0.1);  
    LithoPause(10);  
    LithoTranslate(0, dstep, 1);  
    LithoPause(10);  
    LithoTranslate(0, dstep, 10);  
    LithoPause(10);  
    LithoTranslate(0, dstep, 25); // Rate of translation is changed everytime to keep number of sliding cycles constant  
    LithoSet(lsSetpoint,iload); // Set low normal load for scanning  
    LITHO_END  
}
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