NANOTRIBOLOGY OF VAPOUR-PHASE LUBRICANTS

J. KRIM AND M. ABDELMASOUD

Physics Department, Northeastern University
Boston, MA 02115

Abstract

Vapor-phase lubricants have traditionally been studied within the context of macroscopic system performance. Nonetheless, they may well prove to be of critical importance to the tribological performance of MEMS devices as well since the vapor phase may ultimately prove to be the most effective, if not only, means to deliver and/or replenish a lubricant in certain submicron scale devices. This work discusses how a Scanning Probe Microscope (SPM) can be used in combination with a Quartz Crystal Microbalance (QCM) to investigate the performance of vapor phase lubricants at nanometer length scales.

1. Introduction

Micro-Electro-Mechanical Systems (MEMS) are an emerging, cutting-edge technology which relies on the microfabrication of small scale mechanical components (switches, sensors, mirrors, etc.) and the integration of those components with on-board electronic processing. There is widespread belief that the future is likely to be a world dominated by MEMS and/or NEMS (Nano-Electro-Mechanical Systems) devices, which will be used in such diverse applications as gas and pressure sensors, accelerometers, chemical analytic "microlaboratories", and airborne "nanosatellites". [1] The MEMS of today rely heavily on silicon-based materials and/or fabrication processes which were originally developed for the microelectronics industry. While such processes and materials have yielded working devices, the materials choices are largely historical and may not have resulted in optimal performance and mechanical reliability.

Because MEMS devices must react to mechanical signals, many employ construction topologies that require physical motion. Suspended plates and beams which are fabricated a few microns away from their supporting sub-
strates are in common use, and these structures typically have relatively large areas and very small stiffnesses. These combined characteristics makes MEMS devices highly susceptible to surface forces which can cause the suspended member to deflect towards the substrate; collapse and/or adhere permanently to the substrate. This can happen during device fabrication as well as during normal operation. [2] A number of surface treatments have met with varying degrees of success for alleviating such stiction/adhesion problems, and in these cases friction and wear become the limiting factors to device operational lifetimes. With the current impetus towards device components extending well into the nanometer regime, friction/wear/adhesion complications currently encountered in MEMS devices are expected to be even more severe in NEMS devices due to the enhancement of surface effects as length scales diminish. There is thus a growing need for concomitant studies of the mechanical and tribological properties of sub-micron to molecular-scale systems, and the need to carry out new studies relevant to the development of optimal, or even operational submicron-scale mechanical systems, becomes increasingly pressing.

We discuss here how a Scanning Probe Microscope (SPM) can be used in combination with a Quartz Crystal Microbalance (QCM) for nanometer-scale investigations of the tribological performance of vapor phase lubricants under consideration for MEMS/NEMS devices. Our discussion begins by describing the role of non-lubricated solid-solid contacts in selected MEMS device failures. We then present examples of how a combined SPM/QCM can be used to probe both non-lubricated and vapor-lubricated solid-solid contacts in geometries analogous to those encountered in the actual devices. (Experimental details of the construction of the SPM/QCM apparatus itself are contained in [10]).

2. Failure of MEMS through unlubricated solid-solid contact.

When solid surfaces touch each other, the contact between them occurs predominantly at the summits of the surface roughness. [3] Because each of these contact areas is small, perhaps a few atoms in extent, both the topology and the mechanics of the contacting asperities must be investigated in order to gain basic understanding of the system's overall behavior. If the system itself is of mesoscopic or molecular extent, then an understanding of the nature of such contact zones becomes essential. Solid surface nanocontacts abound among MEMS devices, and a myriad of device complications and failures are associated with them. Here are two representative examples:

The Digital Micromirror Device, or DMD, is a large-scale integrated spatial light modulator which consists of an array of rotatable aluminum
mirrors fabricated using semiconductor-like processing. [4] The array can consist of a million or more independently controlled reflective, digital light switches and, like most other MEMS devices, has contacting surfaces in relative motion. The aluminum-aluminum contacts exhibit friction and wear behavior, and need to be lubricated to prevent their adhesion and permanent bonding. Working devices may be required to operate for up to 10 years and 50,000 operational hours without failure of a single mirror after device shipment! [4] While a wide variety of lubricants have been investigated for use with the DMD, little or no research has been performed concerning the nature of the metal-metal contact itself. Even though aluminum-on-aluminum represents a poor choice of materials in terms of avoiding adhesion, insufficient fundamental knowledge is available to select alternative materials in an informed manner.

An electrostatically actuated micromechanical switch [5] can have superior combinations of parasitic resistance and capacitance as compared with a semiconductor device, even in this day of advanced microelectronics. As such, microfabricated switches and relays could replace both conventional switches and electronic devices in many applications where signal fidelity is crucial and switching speeds are moderate. Although the literature on the performance of these devices is relatively sparse, a number of groups are actively working to fabricate them on account of the anticipated benefits. [6] With the exception of a capacitively coupled microwave switch, [7] the performance of all of these devices is limited by the performance of the contact. [8] The most common failure mechanisms are stiction at the contact point, and progressive degradation of the electrical properties due to unspecified chemical or morphological changes at the contacting interface. Traditional macroscopic approaches to contact improvement have proven irrelevant, since the physical laws which govern the performance at mesoscopic length scales are quite distinct from those of the macroscopic scale. [9] Indeed, it has become evident that the physical nature of the contact must be characterized (which is estimated to consist of approximately ten distinct nanometer-scale asperities [8]) and understood at a fundamental level in order for large device improvements to be achieved.

The metal-metal point-contact problems associated with long-term reliable operation of the DMD and the microswitch are representative of those encountered in a variety of micromechanical devices: A basic understanding of such contacts would be of great use for overall device performance optimization. The adhesion of atomic-scale metal-metal point contacts can be measured in a controlled environment with a scanning probe microscope (SPM) and a quartz crystal microbalance operating in combination [10]. The SPM allows a single asperity contact to be formed, and opens up the possibility of applying and testing existing theories of continuum contact
mechanics with the properties of a nm-scale single-asperity. [11] The microbalance, whose surface is oscillating horizontally, can be employed to measure shear forces associated with the breaking of formed metal contacts, and to monitor the uptake and mechanical properties of adsorbed lubricant species. The shear strength and the work of adhesion are thus two important parameters that can be measured by this technique. The shear strength corresponds to the shear force per unit area required to shear the interface. The work of adhesion corresponds to the energy per unit area required to pull apart the interface.

While it is clear from the preceding discussion that a QCM/SPM can provide powerful information concerning the nature of an un lubricated contact, the major advantages of combining the two techniques are realized upon introduction of a lubricant at the contact. In this case, the QCM can be employed to probe both static (thickness, density, etc...) and dynamic (viscosity, interfacial energy dissipation, etc...) properties of the lubricant that otherwise would be unattainable.

In the sections which follow, we begin with a description of how a QCM acting alone is employed to probe nanotribological properties of potential vapor-phase lubricants. Three examples of joint SPM/QCM capabilities are described in subsequent sections.

3. The Quartz Crystal Microbalance as a Probe of Atomic-scale Mechanical Properties

Studies of the fundamental origins of friction have undergone rapid progress in recent years with the development of new experimental and computational techniques for measuring and simulating friction at atomic length and time scales. [9] Employing established technologies, such as ultra-high vacuum, for the preparation of crystalline samples, nanotribologists have been gathering information in situations where the nature of the contacting surfaces is determined in advance of the measurement. They have collectively measured friction forces per unit true contact area which span twelve orders of magnitude. [9]

[12] If the precise nature of the contacting asperities between macroscopic objects in sliding contact could be determined (such studies do in fact represent an area of high research activity within the tribological community), then the results of nanotribological studies could begin to be directly implemented into mainstream tribological considerations. Meanwhile, the results can be immediately applied to solid-vapor or solid-liquid interfaces, where the complicating factors associated with asperity contacts are less of an issue, and to MEMS/NEMS related issues, where machine components with astoundingly small dimensions are rapidly approaching
the length scales routinely probed by the nanotribological community.

The concept of lubricating high temperature bearing surfaces with organic vapors has a much longer history. It has existed for at least forty years, with substantial efforts beginning in the 1980’s and continuing on to the present day. [13] Vapor phase lubrication occurs via three distinct forms: (a) organic films which are intentionally reacted with a surface to form a lubricating film, (b) vapors which condense to form a lubricating liquid film on the surface of interest, and (c) light weight hydrocarbon vapors deposited onto hot catalytic nickel surfaces. Vapor phase lubricants are advantageous for use at high temperature, (meaning that either the ambient temperature of the entire system is elevated, or the local surface “flash point” temperature due to frictional heating is elevated) and in situations where the vapor can be used as a reservoir for replenishment of areas where the lubricant has been depleted in the course of the bearing lifetime.

Several organic vapors have been identified which exhibit desirable tribological properties, [14] but a detailed and fundamental understanding of their surface chemical reactions in the tribological processes of interest is far from complete. In particular, an understanding of the particular surface reactions which occur, and how they are affected by tribological conditions such as temperature and/or lubricant concentration level in the carrier gas remains inadequate. Ultra-high vacuum and modern nanotribological techniques can be brought to bear on these issues by examining in detail the properties of a known (macroscopic-scale) vapor-phase lubricant, and the knowledge gained (if not the lubricant itself) is extremely likely to be applicable to NEMS/MEMS operations as well. Indeed, the vapor phase may ultimately prove to be the most effective, if not only, means to deliver and/or replenish a lubricant in the case of a submicron scale device. (Alternate approaches which are in development for lubrication of such devices, for example the attachment of a self-assembled monolayers to contacting surfaces, may be more difficult to initially apply, and may be difficult or impossible to replenish if damaged while the device is in operation. Such is not the case for a lubricant applied from the vapor phase, which can reattach itself continuously.)

The Quartz Crystal Microbalance (QCM) is a technique which is particularly amenable to studies of lubricant surface films and/or metal-metal contacting asperities on account of its sensitivity to both the amount of material present as well as the mechanical properties of that material. It has been used for decades for microweighing purposes,[15] and was adapted for atomic-scale friction measurements in 1986-88 by Widom and Krim.[16] [17] A QCM consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor $Q$ near $10^5$. The driving force is kept at constant magnitude at the series resonant frequency of the oscillat
tor, typically in the range \( f = 4 \) to 10 MHz. Each major face is polished to better than optical flatness, and then plated with a metal electrode which is prepared by deposition in ultra-high vacuum (UHV) and can be characterized in situ with Auger electron spectroscopy. In general, the (111) surfaces of metals are studied, and Scanning Tunneling Microscopy (STM) measurements are performed on the surface electrodes to select suitable samples for the measurements of interest.

The quartz crystal microbalance can be an extremely sensitive probe of the mechanical properties of films which may form on its metal electrodes, and/or probe tips which it may come in contact with. In general, all parameters except for the interfacial slippage and viscosity are accounted for in the research discussed here. Measurements of potential lubricant films are carried out in situ by transferring the sample, within the ultra-high vacuum chamber, to a tip which can be cooled to 2K, or alternatively heated to 450 C. Vapor is then admitted to the chamber, producing a change in the resonant frequency of the microbalance which is proportional to the fraction of the mass of the vapor particles which attach to the surface and are able to track its oscillatory motion. (Sensitivities of tenths to hundreths of a monolayer are typical.)

Film adsorption onto the microbalance produces shifts in the frequency of vibration and also the amplitude of vibration if slippage of the adsorbed material is occurring. Amplitude shifts are due to frictional shear forces exerted on the surface electrode by the adsorbed film, or alternatively by a contacting metal asperity. The microbalance in its present arrangement can detect shear forces in excess of \( 2.5 \times 10^{-7} \) N. Characteristic slip times \( \tau \), and friction coefficients (i.e. shear stresses per unit velocity) \( \eta \), are determined via the relations:**

\[
\delta (Q^{-1}) = 4\pi \tau \delta f_o \quad \eta = \frac{\rho_2}{\tau}
\]

(1)

where \( \rho_2 \) is the mass per unit area of the adsorbate, and \( \tau \) corresponds to the time for an object’s speed to fall to 1/e of its original value, assuming that it has been pushed at constant speed and then released, allowing frictional forces to bring it to a stop. (Amplitude shifts are converted to quality factor shifts \( \delta (Q^{-1}) \) through calibration with a gas which does not condense at the temperature of interest.) The “object” of interest is the film which is adsorbed on the oscillatory substrate, and \( \tau \) represents an average over all film particles. Substantial decoupling effects occur whenever the slip time exceeds the period of oscillation. Partial decoupling is also quite evident for values of \( \omega \tau = 2\pi f_o \tau \geq .5 \) where the percent of film mass which effectively couples to the oscillation is 80% or less.

If the adsorbed material is more than molecularly thick, then the oscillating surface can in principle generate plane-parallel motion in the con-
tacting material. The response of the oscillator in such conditions depends critically on the internal motion of the film adjacent to the electrode, as well as on whether slippage is occurring at the interface with the substrate. A variety of models have been developed to predict the oscillator response in a such an environment, incorporating the possibility of, among other things, liquid-like viscosity, multilayered structures and interfacial slip. [18] [19] [20] In the event that any of the the lubricant films to be studies exhibits such slippage/viscoelastic effects, the behaviors will be readily observable.

4. Example 1: Molecular-scale investigations of vapors which are known to lubricate at the macroscopic scale

As mentioned earlier, a variety of organic vapors have been identified which exhibit desirable tribological properties,[14] but a detailed and fundamental understanding of their surface chemical reactions in the tribological processes of interest is far from complete. In particular, an understanding of the particular surface reactions which occur, and how they are affected by tribological conditions such as temperature and/or lubricant concentration level in the carrier gas remains inadequate. In an entirely analogous manner, lubricant materials are being utilized on current MEMS devices based primarily on performance, with incomplete understanding of the manner in which the lubricant functions at a molecular level.

As an example, we discuss here how nanotribological characterizations of a particular (macroscopic) lubricant, phenyl phosphate-based TBPP, could aid tribological performance of both macroscopic and nanometer-scale devices. This vapor-phase lubricant consists of a blend of tertiary-butyl phenyl phosphate (TBPP) molecules,[21] whose atomic constituents are carbon, hydrogen, oxygen and phosphorus. It demonstrates high quality performance at elevated temperatures [13] and exhibits oxidation inhibiting characteristics as well as a number of other desirable tribological properties, particularly when iron is present. While the precise mechanisms for its beneficial properties are uncertain, it is believed that after reacting with the surface, the phosphate contained in the original lubricant molecule acts as a binder for graphitic carbon, which in turn may be the actual lubricant. The tribological properties of TBPP are highly sensitive to its concentration levels in the carrier gas material, presumably due to a balance between the reaction rate of the vapor with the surface and the rate at which the lubricant is depleted in a particular setting.

The oxidation inhibiting properties of TBPP are presumably due to preferential adsorption of TBPP molecules over oxygen molecules, but this has not been established in a controlled environment. Assuming the phosphate binding mechanism to be valid, then a phosphate-free lubricant should
exhibit markedly different tribological properties. Moreover, since the presence of iron is known to enhance the lubricating properties of TPBB, its behavior on a nonferrous substrate is expected to be distinct.

In order to examine these issues, detailed examinations of TBPP could be performed in a very straightforward manner with a joint QCM/SPM apparatus, where the electrodes of the QCM and the tip of the SPM are composed of the materials of relevance to the device performance:
(1) Measurements of the uptake rate of the lubricant as a function of exposure rate and substrate temperature (a QCM can be successfully operated up to 500°C) [22] to aid in our understanding of the sensitivity of the lubricant to concentration rates.
(2) Measurements of the oxygen uptake rate of the metal surface, to examine whether the lubricant is indeed preferentially bound to the metal surface.
(3) Auger electron spectroscopy measurements of the surface at various stages of uptake of the reactive lubricant, for monitoring of the chemical composition of the surface, for example its graphitic carbon content.
(4) Measurements of the mechanical properties of the lubricating film, in the event that slippage and/or film viscosity can be detected in response to the oscillatory motion of the QCM electrode (as described in an earlier section).
(5) SPM measurements of the lubricant surface, to determining both molecular structure and larger scale surface morphology as a function of overall film thickness, and in particular to determine whether graphitic carbon is present at the surface.
(6) SPM/QCM measurements of the drag force of the SPM tip on the oscillating QCM surface electrode.

We note that analogous studies could be performed on vapors which are known to lubricate MEMS devices to understand the lubricating mechanisms involved. Moreover, there may exist lubricants which exhibit desirable tribological characteristics for both macroscopic and microscopic device applications.

5. Example 2: Nanomechanical properties of potential lubricants

In addition to probing the molecular-scale properties of vapors which are known lubricants, a combined SPM/QCM is itself a simple nanometer-scale mechanical system whose response to vapor-phase adsorbents can be monitored for nanotribological performance. In particular, the apparatus can be employed to examine the effect of the rubbing action of the scan tip on the QCM can induce tribochemical reactions which result in the formation of reaction products with desirable tribological properties. As an example, we
assume graphitic carbon to have desirable tribological properties [23] and discuss the particular case of ethylene/platinum.

The tribological properties of ethylene/Pt are unsubstantiated. Nonetheless, its temperature dependence and structure has been thoroughly characterized by the surface science community. The adsorption and reaction products of ethylene adsorbed in ultra high vacuum conditions (UHV) on Pt(111) have been characterized by a wide variety of surface science techniques. [24] These studies have determined that ethylene (C\textsubscript{2}H\textsubscript{4}) bonds molecularly to the Pt surface at temperatures up to about 200K. Beginning at about 230K, ethylidyne (C-CH\textsubscript{3}) is formed by loss of hydrogen and this species is stable up to 430K. Upon annealing above 430 K, further dehydrogenation occurs until, above 700K, only carbon is left on the surface. Annealing this carbon covered surface to temperatures above 800 K results in the formation of graphite islands on the Pt surface. The entire sequence can be imaged and identified by STM. Although the formation of graphitic carbon on an open Pt surface occurs at elevated temperatures, it may well occur at much reduced temperatures in the presence of a sliding contact, where “flash point” temperatures are frequently much higher than ambient.

The following studies could be performed on this potential lubricant, where the SPM is taken as a scanning tunneling microscope employed for atomic-scale surface characterizations of morphology or chemical species identification. The QCM is utilized for simultaneous measurements of the dynamical properties of the adsorbed species and to measure the drag force which the SPM tip exerts on the surface of the QCM surface when the QCM is oscillating.

A QCM with Pt(111) electrodes can be dosed with ethylene in UHV conditions and the frequency and quality factor shifts of the microbalance upon uptake of the gas will be monitored to determine the ethylene film’s mass per unit area and dynamical properties. The QCM oscillatory motion can then be halted, to allow the surface to be imaged with the STM in order to identify the structure of the chemical species which is present at the tip-substrate interface. The QCM then resumes its (horizontal) oscillation with a STM tip in (tunneling) contact with the surface, allowing tip-surface sliding speeds to be achieved (up to 10 cm/s) which are as much as five orders of magnitude greater than those typical of STM scans on stationary surfaces. The QCM frequency and amplitude during this process are monitored to measure the drag force of the STM tip along the surface, a parameter which is likely to be chemically sensitive. The oscillation will then be halted and the surface reimaged investigate whether the same chemical species is still present or whether a tribologically induced reaction has occurred, the most likely reaction product being graphitic carbon.

By performing such experiments at varying tip-substrate sliding speeds,
sliding times and temperatures, a sliding speed vs. interfacial contact temperature vs. sliding time phase diagram can be mapped out. Repeating the measurements with a friction force microscope rather than an STM would in addition allow for investigations of the lateral force as a function of the normal force applied to the scan tip.

6. Example 3: Sliding friction/molecular transport

The increased recent interest in the fundamental origins of friction has sparked a variety of discussions and debates concerning the nature of the atomic-scale mechanisms which dominate the dissipative process by which mechanical energy is transformed into heat. While much recent attention has focused on phonon contributions to friction on account of the relative ease with which atomic lattice vibrations can be modelled by molecular dynamics simulations, [25] Electronic mechanisms for friction due to sliding-induced excitations of conduction electrons at metallic interfaces have also been put forward. Such mechanisms are quite distinct from the friction associated with static charge buildup, a theoretical problem which, from Coulomb's original work on friction until the present time, remains unsolved.

We have recently observed direct experimental evidence for electronic contributions to friction [26] by investigating the friction associated with sliding of an arbitrary material (nitrogen) along an arbitrary superconductor (lead) above and below the metal's superconducting transition temperature. We observed the friction associated with nitrogen sliding over lead in its superconducting state to be approximately half that observed for its normal state. The reduction in friction is best explained in terms of an abrupt drop in conduction electron contributions to the friction when the lead enters the superconducting state, leaving phonon excitations as the sole probable mechanism for energy dissipation. The result implies that a variety of intriguing applications may be possible, in those systems where electronic contributions are found to be significant. For example, systems characterized by substantial enough electronic friction forces would allow surface transport of adsorbed atoms or molecules via the drag forces exerted by an electrical current. The surface transport might be employed for delivery of lubricant molecules, or for transport of molecule which have been chemically modified by a SPM to a specified collection point.

These particular applications are perhaps years away. Nonetheless, they demonstrate how our current knowledge of friction at the atomic scale can allow us to be able to predict, at the fundamental level, which interfaces will be characterized by reduced friction levels.

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References

[23] We emphasize that this is an assumption, and not an established nanotribology result.
