FINAL TECHNICAL REPORT

Project Title:	Development and Integration of Single-Asperity Nanotribology Experiments & Nanoscale Interface Finite Element Modeling For Prediction and Control of Friction and Damage in Micro- and Nano- Mechnical Systems
Prepared By:	Robert W Carpick, Principal Investigator
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Recipient:	University of Wisconsin-Madison Department of Engineering Physics 1500 University Ave. Madison, WI 53706
DOE Project Director:	Timothy J. Fitzsimmons
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Final Report on Work Accomplished Under Current DOE BES Grant, 9/15/02 – 8/14/06

1. Research Activities

1.1 Project Goals

The goals of the grant were: (1) to measure fundamental tribological properties of nano-scale single asperity contacts between materials relevant to micro- and nano-mechanical systems using atomic force microscopy (AFM), and (2) to analyze the successes and shortcomings of the wide array of existing models of rough surfaces in contact, and then to fill in the gaps by developing a versatile new computational model of contact and friction that is applicable to actual complex device surfaces. Indeed, one of our major findings is that no current models sufficiently described the characteristics of the surfaces we are studying.

The materials targeted initially were: (1) silicon-based materials used in leading-edge surface micromachined devices, namely silicon and silicon oxide with specific self-assembled monolayer lubricant surface treatments; and (2) ultrananocrystalline diamond (UNCD) thin films with a variety of surface treatments, which have outstanding mechanical properties and are under investigation for a wide range of device applications. The investigations were widened to include diamond-like carbon (DLC), near-frictionless carbon (NFC), nanocrystalline diamond (NCD), and tetrahedral amorphous carbon (ta-C), as well as graphite and diamond reference samples to lead to a comprehensive array of the most important carbon-based films that exist. Initial results on these samples have been obtained, while most progress was made studying UNCD.

A key related goal was to collaborate with researchers at Sandia to compare our results to larger scale tribological measurements of the same materials, specifically self-assembled monolayer (SAM)-coated silicon surfaces, subjected to *in-situ* tribological testing in a Sandia MEMS actuator device known as the *Nanotractor*.

1.2. Discoveries

1.2.1 Studies of SAM Films[1-5]. We have discovered new connections between specific properties of the surfaces of the materials under study and their nanotribological characteristics This provides new, basic insight into the underlying mechanisms of friction at the molecular scale. These results naturally lead to new nano-scale constitutive laws for use by an interfacial contact model that can predict contact area, contact stresses, adhesion, and friction of multi-asperity interfaces that are relevant to a wide range of micro- and nano-mechanical devices.

First, collaborative studies with Sandia were carried out to investigate the fundamental characteristics of friction in an actual silicon MEMS device. Studies were conducted with a device designed at Sandia called the *nanotractor* which is discussed in further detail in Section II. The device can be fabricated with uncoated surfaces (*i.e.* the native silicon oxide) or with SAM coatings, including two linear hydrocarbons, octadecyl-trichlorosilane (chemical formula: $C_{18}H_{37}SiCl_3$, abbreviation: ODTS) and octadecene (chemical formula: $C_{18}H_{36}$, abbreviation: OD), and a linear fluorinated molecule, tridecafluoro-1,1,2,2-tetrahydrooctyl)tris-(dimethylamino)-silane (chemical formula: $CF_3(CF_2)_5(CH_2)_2Si(N(CH_3)_2)_3$, abbreviation: FOTAS). These are discussed in more detail and illustrated in Section II.

We showed that the nanotractor is a promising vehicle for *in-situ* friction and wear studies of MEMS. Although more experiments are needed and further development of the testing methodology is required, several initial conclusions can be made:

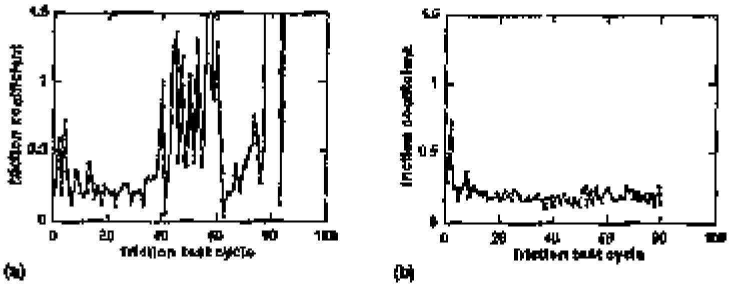


Fig. A Variation of friction coefficient with number of friction tests performed for two Nanotractor samples. (a) Friction coefficient *vs.* number of test cycles for an oxide-coated surface (no SAM coating). (b) Friction coefficient *vs.* number of test cycles for a FOTAS monolayer-coated surface, showing dramatically improved performance.

- The nanotractor typically fails via interfacial seizure due to wear processes at the sliding interfaces under well-characterized loading conditions.
- Tests conducted under moderately low apparent pressures (<50 kPa) lead to noticeable wear of the polysilicon surface was observed.
- A monolayer lubricant significantly enhances the wear resistance and frictional properties of MEMS surfaces (Fig. A). ODTS exhibits the lowest friction coefficient, while FOTAS exhibits the best wear performance
- Small changes in surface roughness have an affect wear properties, but not as large an effect as the monolayer coatings have.
- The friction coefficient can vary substantially long before failure, and before device performance (such as travel distance) is altered.
- The atomic force microscope (AFM) can be applied to study surface modification without dissembling the nanotractor device, because of the large travel distances (>20 μm) that the nanotractor undergoes during a wear test, leaving an exposed wear track for investigation. Therefore, in future studies it should be possible to conduct wear and AFM tests sequentially on the same device to follow the evolving topography.

Investigations were performed in parallel to determine the nanoscale frictional properties of the alkylsilane monolayers using AFM. These monolayers are commonly used in MEMS to reduce adhesion and friction. Three different SAMs on silicon, which are described in more detail in Section II, were compared: (ODTS), octadecene (OD), and (FOTAS).

For the ODTS monolayer there are two phases evident; the liquid condensed phase shows measurably lower friction at low loads than the liquid expanded phase (Fig. B), demonstrating that lower friction is associated with higher packing density of the molecules. In addition, reproducibility is improved when using SAM-coated tips as compared to uncoated tips. For the FOTAS monolayer, reproducibility of friction and adhesion measurements depends on the scanning history of the tip. These results indicate that transfer of SAM molecules or other contaminants to uncoated tips is common phenomenon, and has a significant effect on the measured friction and adhesion forces. This has wider importance for the acquisition of reproducible AFM nanotribology measurements in general, and strongly suggests that AFM researchers should strive to characterize and control the chemistry and structure of their tips

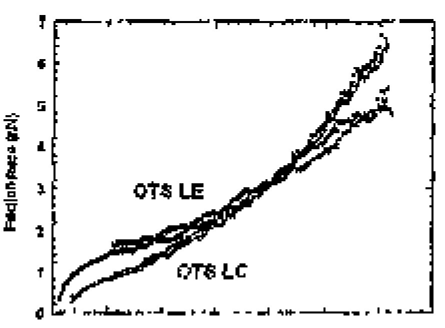


Fig. B. A friction vs load plot for the ODTS monolayer for the different phase regions using an ODTS-coated AFM tip.

to obtain meaningful measurements. Also we see that adhesion is slightly lower for FOTAS compared to ODTS, but friction increases more rapidly, leading to higher friction at higher loads, in agreement with actual MEMS measurements.

1.2.2 Studies of Carbon-Based Thin Films

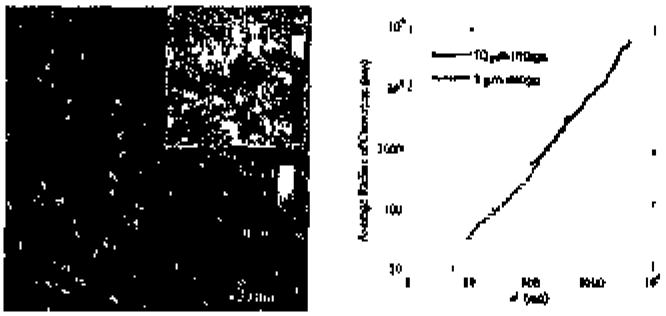
Chemical optimization of the UNCD surface to control tribology at the nanoscale[6-9]. In micro and nano-scale devices, friction due to high adhesive forces (stiction) is the main cause of failure due to increased surface to volume ratio. In our studies on UNCD thin films, we have shown for the first time that UNCD surfaces can be tailored at the atomic scale to reduce adhesion to the van der Waals' limit, indistinguishable both chemically and adhesively from single crystal diamond. To achieve this goal, we devised a new methodology to look at the *underside* of the UNCD film by etching away the substrate and modifying its surface chemistry by hydrogen termination. By using atomic force microscopy, we measured adhesion and friction on UNCD surfaces, and by using synchrotron X-ray spectroscopy techniques we confirmed the bonding configuration and chemical state responsible for such a low adhesion. Our methodology is not only applicable to diamond-based MEMS devices but could very well be extended to all thin film materials, including Si and SiC.

Micro and nano-scale wear analysis using X-PEEM-NEXAFS spectromicroscopy[8,10]. X-PEEM/NEXAFS allows one to take a high-resolution photoelectron microscope image of a sample and simultaneously perform spatially-resolved (50 nm or better) chemical spectroscopy using NEXAFS. In this case, a wear track produced on the UNCD surface by pin-on-disc type wear testing apparatus is analyzed. The analysis of the wear tack shows the presence of oxygen and Si sub-oxides in the wear track, indicating that a transfer layer was formed by the wearing of the Si_3N_4 ball against UNCD. These kind of studies provide invaluable insight into the robustness and reliability of UNCD as a structural material for advanced MEMS devices.

Diamond like carbon (DLC) thin films[11-13]. DLC films are attractive for MEMS applications because of their mechanical and frictional properties. More importantly, the deposition process is simple, easily scalable and works at room temperature. We have looked at variety of DLC films with high and low hydrogen content and as well as with dopants such as fluorine and Si. The highlights of results are summarized below:

- We have shown that for the self-mated tetrahedral amorphous carbon (ta-C) interface, the measured adhesion values are equivalent to those of single crystal diamond.
- The low adhesion values are stable even after annealing these films in vacuum at ~800 ^{0}C. These finding are very important for applications which require low friction and adhesion at high temperatures.
- NEXAFS studies on thermally annealed ta-C films at high temperatures has shown indications of structural transformations leading to overall increase in sp^2-bonded carbon content in the film. These finding are very important in the context of understanding physics of stress relief behavior and its relation with bonding rearrangement in these films.
- Si incorporated DLC found to be more stable as compared to F incorporated DLC when annealed in air at temperatures ~300^{0}C

1.2.3 Modeling and Simulation[14-16,3]. We have developed a "summit search" method to investigate the geometry of summits at different length scales of surfaces imaged by atomic force microscopy (AFM). In this method, the height of each sample point (pixel) of a surface is compared to the heights of all neighboring sample points that are within a square region with size



(a) (b)

Fig. C. (a) 512x512 pixel AFM images of the same region of a polycrystalline silicon surface with RMS roughness ~ 3 nm, taken at 10 μm and 1 μm (inset) scan sizes. (b) The images in (a) are analyzed to determine the average radius of curvature using a summit search algorithm wherein a pixel of an AFM image is determined to be a summit (with an associated radius of curvature) if its height is greater than the heights of all neighboring pixels within a distance d/2. This plot shows that the summits for the surface become increasingly sharper as the neighborhood size d decreases, indicating that measures such as number of asperities per area, average asperity height and average asperity curvature are scale dependent.

d by *d*. When a summit is found, we compute its radius of curvature, with the results (averaged over the specimen) shown in Fig. C.

These results show that summit density, height, and curvature of AFM images of actual silicon MEMS surfaces have a power law relationship with the sampling size *d* used to define a summit, and most importantly, no well-defined value for any of these measures is found, even at the smallest experimentally accessible length scale. This behavior, and its similarity to results for fractal Weierstrass-Mandelbrot (W-M) function approximations, indicate that a multiscale model is required to properly describe these surfaces. Indeed, our method may provide for more straightforward determination of fractal dimension than the power spectral density method.

A multiscale contact model is developed using a surface having numerous length scales for roughness wherein the smaller roughness scales are successively modeled as asperities that are superposed on the asperities of the next larger scale. With this model, the total contact area predicted with elastic Hertz single asperity behavior approaches a limit with increasing number of roughness scales. Furthermore, when the scale-dependence of the heights and radii for AFM images are used, as obtained from our summit analysis method, the contact area calculated does not depend on the scaling ratio that separates roughness scales. This is important as it shows that a simpler surface representation with large scale constants and fewer scales is valid.

2. Estimate of the Unobligated Balance

As required by DOE, we have estimated the unexpended funds that will remain at the end of the current project period (9/15/05). Based on our current spending rates and obligations, we estimate this amount to be zero.

3. Output, Collaborations, and Personnel

Our initial proposal, grant DE-FG02-02ER46016, entitled *Development and integration of single-asperity nanotribology experiments and nanoscale interface finite element modeling for prediction and control of friction and damage in micro- and nano-mechanical systems*, commenced on 9/15/02. The PIs have been extremely productive, with substantial new discoveries made, several collaborations catalyzed, and multiple personnel supported.

3.1. Dissemination: Papers and Presentations

Work stemming directly from this funding has been presented so far in five published peer-reviewed journal articles, two peer-reviewed conference proceedings papers, and six additional conference proceedings papers. One further peer-reviewed journal article has resulted partially from this support. There are 9 further papers in advanced stages of preparation for peer-reviewed journals. High-impact articles have also been partially enabled by this grant. the PI authored an invited book chapter in the *Handbook of Nanotechnology*, and has accepted an invitation to co-author a review article in *Mat. Sci. Eng. Reports*. During the grant period, our results have directly attracted over 40 invited talks at national and international meetings and university, industry, and lab settings by the PIs and in some cases by their personnel. An additional 28 contributed talks have been presented by the personnel supported by this grant. The complete details of these papers and presentations are listed in the Appendix.

3.2. New Basic Science Collaborations and Projects Catalyzed

This significant output has been aided substantially by several synergistic collaborations that this grant catalyzed. An active collaboration with researchers at Sandia National Laboratories who study MEMS tribology and modeling has flourished, and is discussed further in the Project Description below The research has been closely coordinated (see *Research Discoveries* below) The PI's participated in a synergistic Sandia LDRD project with these researchers entitled "High Fidelity Frictional Models for MEMs," and a small subcontract to UW-Madison from this project was provided from 2002-2004. The PI participated by invitation with two DOE "Center of Excellence for the Synthesis and Processing of Advanced Materials" (CSP) programs entitled "Carbon-based Nanostructured Materials" and "Experimental and Computational Lubrication at the Nanoscale". The PI also successfully proposed two user proposals for DOE "Nano-Centers", specifically through the Center for Integrated Nanotechnologies (CINT) at Sandia National Laboratories (collaborating PI· Dr. M. Chandross) and through the Center for Nanoscale Materials (CNM) at Argonne National Laboratories (collaborating PI· Dr. J.A. Carlisle) In the case of the CINT proposal, this resulted in a grant of $40,000 provided to the Sandia researcher, Dr. Chandross, to support his work on the collaboration A new collaboration, between co-PI Plesha and T. Vogler of Sandia National Laboratories has begun on the physics of high speed behavior of particulate materials, where the main issues are particle-particle friction and particle-solid media interaction, as well as compuational modeling. Presently these investigators have pending a Sandia LDRD proposal entitled "New techniques for modeling dynamic behavior of powdered materials".

The collaborations have involved several DOE researchers: Dr. A Erdemir, Dr. J.A. Carlisle, and Dr. O. Auciello (Argonne National Laboratories), and Dr. T A. Friedmann, Dr. M.P. de Boer, Dr. M. Chandross, Dr. E.D. Reedy, Dr. T. Vogler and Dr D. Segalman (Sandia National Laboratories).

Collaborations with other university-based researchers have also resulted from this work: Prof. W.T. Tysoe (University of Wisconsin – Milwaukee; topic. macroscopic UHV tribometry of near-frictionless carbon), Prof. W G. Sawyer (University of Florida; topic· modeling and experiments on rough surfaces), Prof. G. Swain (Michigan State University; topic. boron-doped nanocrystalline diamond).

New collaborations with faculty at the PI's institution, the University of Wisconsin-Madison, have also been catalyzed by the DOE funding. This includes: Prof. I. Szlufarska (topic· Molecular Dynamics simulations of friction), Prof. G. De Stasio (topic: high resolution spectromicroscopy of tribological interfaces), Prof. J.E Lawler (topic: use of plasmas for carbon film growth), Dr. Kumar Sridharan (topic: synthesis and tribological characterization of diamond-like carbon via plasma ion immersion technology), and Prof. D. Kammer (with Dr. D. Segalman of Sandia National Laboratories) on the topic of frictional energy dissipation as a source of damping in structural vibrations.

The collaborations catalyzed by this grant have led to the submission of several proposals to other agencies. These new initiatives are in the general area of nanotribology and nanomechanics of surfaces and serve to enhance the level of activity and discovery in these areas, with potential synergistic benefit to DOE priorities.

Also thanks to this grant, we have become new users of a major DOE user facility, the Advanced Light Source at Berkeley. We are conducting X-ray absorption and photoemission spectromicroscopy experiments there.

3.3. Industrial Collaborations

Three industrial collaborations have also been catalyzed directly as a result of this DOE grant. We are collaborating with Advanced Diamond Technologies, Inc. (ADT) on the characterization of wear-resistant ultrananocrystalline diamond. We assisted ADT with some consulting that resulted in a successful SBIR grant awarded to ADT. A small subcontract from that award was made to our group for this applied characterization work which built on the basic research work carried out under the DOE grant. We are also interacting with 3M Corporation, who provided the PI with an "Untenured Faculty Award". Through collaboration with 3M research scientist Dr. T. Dunbar, we chose to devote these funds to a study of the frictional properties of alkanephosphonate self assembled monolayers. This study complements the work on silane monolayers that is being carried out under the DOE grant and has provided additional insights to the tribological properties of these systems. Finally, a collaboration with Prof. Frank Pfefferkorn has led to the submission of a proposal for an "Industrial & Economic Development Research Program" grant from the State of Wisconsin (pending). The grant would fund a combination of basic and applied research in collaboration with Performance Micro Tool, Janesville, WI, to study the application of nanocrystalline diamond coatings to the surfaces of high-performance micro-endmill tools. The goal is to develop coatings that minimize wear and energy consumption during precision machining operations.

3.4. Human Resource Development

The current grant have been used to support salary for PIs Carpick and Plesha. This was combined with funds from other grants to provide summer salary to eliminate the need for summer teaching. This enabled a substantial amount of time to be devoted to the research.

Three graduates students were supported directly or indirectly by the current grant: Mr. C. Bora (advisor: Plesha), Mr. D. Grierson (advisor: Carpick), and Ms. E. Flater (advisor: Carpick). Ms. Flater's support was primarily provided by a NSF Graduate Fellowship, and by the LDRD project from Sandia mentioned above. We note that Ms. Flater won a Best Poster Award, 25th AVS Annual Symposium on Surface Analysis (June 2003).

These three students all began their Ph.D. research during the initial grant period, and have all made substantial progress toward their goal. All have passed their initial department Qualifying Examination, their Ph.D. Preliminary Examination. Dr. Flater graduated with her Ph.D. in April 2006, and began a faculty position as an Assistant Professor in the Physics Dept of Luther College, Iowa. During the course of the grant, Dr. Flater spent one month at Sandia National Laboratories in the summer of 2003 working in the lab of our collaborator, Dr. M.P. de Boer, on MEMS tribology measurements. This resulted in a publication and new aspects to the research.

A postdoctoral researcher was also hired and supported by this grant. In recognition of his strong background and impressive progress and initiative, Dr. Anirudha V. Sumant was subsequently promoted to the status of Assistant Scientist (staff scientist) at UW-Madison in November, 2003. Dr. Sumant is an expert in semiconductor and diamond film synthesis and characterization and has helped to catalyze many of the ideas pursued in this work. He subsequently was hired at Argonne National Laboratories as an Assistant Materials Scientist in the Center for Nanoscale Materials.

Several undergraduates have been supported directly or partially by this grant, and have gained valuable research experience. Most notably, Mr. Mark Street (B.Sc., Engineering Mechanics, 2006) devoted over a year of work to the project, culminating in a summer research project conducted at Sandia National Laboratories in the summer of 2004, again working in the lab of our collaborator, Dr. M.P. de Boer on MEMS tribology measurements. Another undergraduate student, Mr. Graham Wabiszewski, conducted over a year of research on the grant. He has now become a Ph.D. student at the University of Pennsylvania, Dept. of Mechanical Engineering and Applied Mechanics. Three other undergraduates have conducted work on this project, including two students who devoted their senior research thesis project to topics related to this grant. One of those, Mr. Jason Bares, is now a Ph.D. student at the University of Florida, Dept. of Materials Science.

Finally, during the course of this grant, Prof. Carpick was recommended for promotion to Associate Professor with Tenure. He has since re-located to the University of Pennsylvania, Dept. of Mechanical Engineering and Applied Mechanics, effective 1/1/2007.

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