REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 09-11-2006	**2. REPORT TYPE** Final Report	**3. DATES COVERED** *(From - To)* 1 Sept 04 - 15 Aug 06

4. TITLE AND SUBTITLE
Miniaturization Science for Space: Lubrication of Micro-Electro-Mechanical Systems (MEMS) for Space Environments

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-04-1-0113

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Perry, Scott, PhD

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Houston
4800 Calhoun
Houston, TX 77204-2015

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Maj Jennifer Gresham
Air Force Office of Scientific Research
875 N. Randolph St, Ste 325
Arlington, VA 22203-1768

10. SPONSOR/MONITOR'S ACRONYM(S)
AFOSR/NA

11.
AFRL-SR-AR-TR-06-0480

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: Approved for Public Release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
In this study, the vapor phase lubrication of interacting gold surfaces has been investigated on the atomic and molecular level using the quartz crystal microbalance (QCM), atomic force microscopy (AFM) and scanning tunneling microscopy (STM). These techniques have provided a fundamental understanding of the molecular nature of adsorption, adhesion, and current flow occurring at gold interfaces through the formation of self-assembled monolayers of conjugated aromatic thiol molecules. The issues of static adhesion and contact performance have been addressed simultaneously in relation to the nature and composition of the interface. Maps of both current and adhesion demonstrated the potential of using conjugated species with fluorine substituents on the basis of their tribological and electrical behavior as candidates for lubricating Au/Au interfaces in MEMS devices. Although they do not form a closely-packed geometry compared to *n*-alkanethiol SAMs, they however provide hydrophobic,"Teflon-like" surfaces which accounts for the observed low adhesion.

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15. SUBJECT TERMS
Atomic force microscopy (AFM), thiol molecules, quartz crystal microbalance

16. SECURITY CLASSIFICATION OF: UNCLASSIFIED			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Scott Perry, PhD
a. REPORT unclassified	**b. ABSTRACT** unclassified	**c. THIS PAGE** unclassified	UU	11	**19b. TELEPHONE NUMBER** *(include area code)* (713) 743-9240

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Final Technical Report

Air Force Grant # FA9550-04-1-0113

Miniaturization Science for Space: Lubrication of Micro-Electro-Mechanical Systems (MEMS) for Space Environments

For the period: *(09/01/04-8/14/06)*
Contract initiation date: 03/01/04

Principal Investigator

Scott S. Perry
Department of Chemistry
University of Houston
Houston, TX 77204-5641

Cognizant Program Manager

Maj. Jennifer Gresham, Ph.D.
AFOSR/NL
801 North Randolph Street
Arlington, VA 22203-1977
(703)-696-7787

2. Objectives (as described in the original proposal):

The *objective* of the proposed research program is to determine the effects of a space environment on several potential lubrication schemes for MEMS technology. This program is investigating an array of candidate component materials and lubrication schemes with respect to their performance under variable temperature and pressure (vacuum) conditions. Specifically, experiments have involved atomically clean surfaces of silicon, silicon nitride, as well as surfaces of their respective native oxides, diamond like carbon, and silicon carbide. Lubrication methods have entailed chemical modification of the surfaces through the introduction of thin lubricant films in the form of self-assembled monolayers, and a novel vapor phase lubrication scheme. The experimental approach for characterizing the effects of space environments listed above entails the correlated measurement of surface chemical composition and interfacial friction and adhesion. In order to insure relevance to MEMs applications, the measurements are being conducted on the submicron scale with atomic force microscopy (AFM). Relevance to space applications is generated through the use of a novel variable-temperature, ultrahigh vacuum (UHV) AFM for tribological measurements. Recent investigations have aimed to establish the correlation between molecular order and density in the leading tribological candidate system entailing self-assembly of alkane chains on silicon substrates. While there is widespread discussion of such an approach, little effort has been made to establish detailed protocols for the procedure. In the absence of such efforts, wide variability in performance is to be expected. Attention is now being turned to potential solutions for vapor phase lubrication of MEMS-based RF switches.

3. Status of Effort:

This report documents experiments conducted during the previous twelve months of the program. During this most recent period, the program has focused on the mechanism of attachment of self-assembled monolayers on gold surfaces and the influence of such procedures on their tribological properties. In addition, significant effort has been aimed at the development and construction of a quartz crystal microbalance (QCM) and associated gas chambers for the investigation of potential vapor phase lubrication schemes designed for use with MEMS-based RF switches. In addition, results from QCM and AFM measurements have been closely correlated with detailed chemical composition data obtained from X-ray photoelectron spectroscopy data. The progress of these efforts is described in the following section.

4. Accomplishments/New Findings (09/01/04-8/31/05)

4.1 Overview of Contact Current and Adhesion Studies

SAMs of five different thiol molecules have been deposited from the vapor phase and studied in an effort to understand the self-assembly process. Furthermore, this investigation aims to simultaneously address the issues of static adhesion and contact resistance between metal surfaces. The structures of the molecules of interest are shown in Figure 1. Fluorinated species are of special interest because of their known ability to reduce friction and friction between metal surfaces. First, in order to detect the existence of a molecular monolayer, the Quartz Crystal Microbalance (QCM) was used to measure the percent coverage of each SAM. Next, to understand the extent of ordering of the thiol molecules and the quality of SAMs water contact angles were measured using a goniometer. X-ray Photoelectron Spectroscopy (XPS) was employed to determine the actual chemical composition of the SAMs and estimate the film thickness.

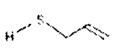
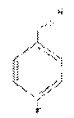
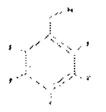
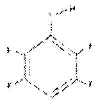
Name of Compound	Structure	Name of Compound	Structure
Allyl mercaptan C_3H_6S		**4-fluorophenyl methanethiol** C_7H_7FS	
2,3,4,5,6-pentafluoro benzenethiol C_6HF_5S		**3-chloropropane-1-thiol** C_3H_7ClS	
2,3,5,6-tetrafluoro benzenethiol $C_6H_2F_4S$			

Figure 1. Thiol molecules of interest.

4.2 Mass Uptake Measurements with QCM

Analysis of our QCM data was based on a theoretical mass of the monolayer. This mass was based on the assumption that one thiol molecule occupied a $(\sqrt{3}\,x\,\sqrt{3})R30^o$ area with respect to the gold lattice. Previous studies have shown that long chain *n*-alkanethiols adsorb on the Au(111) surface in a $(\sqrt{3}\,x\,\sqrt{3})R30^o$ structure. Additionally, the experimental mass of the monolayer could be calculated using the Sauerbrey equation and by recalling that the area of gold on the quartz crystal is 39 mm^2. Thus, the expected mass uptake is given by the following equation:

$$Monolayer\ Mass = 1\ thiol\ molecule\ x\ \frac{39\,mm^2 active\ area\ of\ Au}{0.25\,nm^2\ thiol\ unit\ cell}\ x\ \frac{FW\ of\ thiol}{Avogadro's\ Number}$$

Vapor uptake experiments with the QCM showed irreversible binding of thiol molecules to Au, as evidenced by the formation of a plateau in the mass uptake curve as saturation coverage was reached (Figure 2). Adsorption of short-chain allyl mercaptan (C_3H_6S) exceeded the theoretical saturation coverage. This anomalous short chain adsorption is rationalized in terms of multilayer formation, consistent with previous work done in this laboratory (unpublished results) on short-chain *n*-alkanethiols (C_2H_6S and $C_4H_{10}S$). However, halogenated short-chain thiols (represented by 3-chloropropane-1-thiol) did not show evidence of multilayer formation possibly due to steric hindrance from the bulky chlorine substituent. In the case of fluorine substituted aromatic thiols, results have shown that the percent coverage varies systematically as a function of number of fluorine substituents. As the number of fluorine substituents increases, the percent saturation coverage decreases.

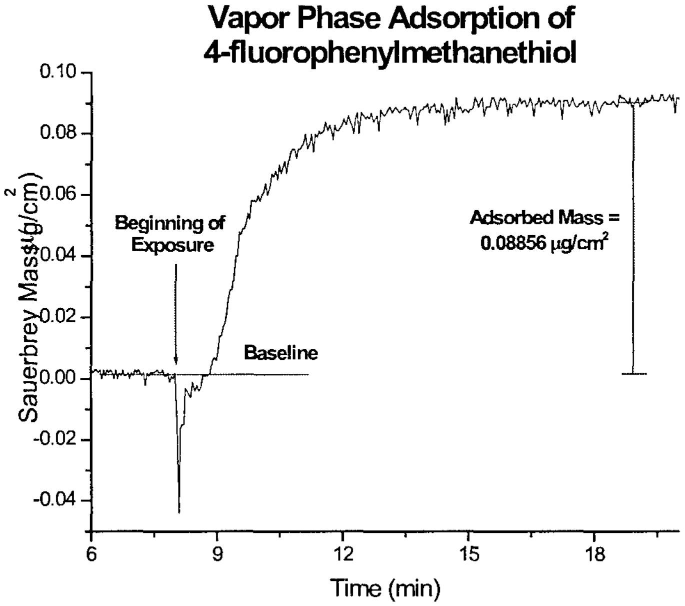


Figure 2. QCM measurement of vapor phase uptake of potential lubricant molecule.

Thiol SAMs	Theoretical Mass (ng)	Experimental Mass (ng)	Percent Coverage
Allyl mercaptan	19.2	47.2	246%
3-chloro-1-propanethiol	28.6	23.1	81%
4-fluorophenylmethanethiol	36.8	34.5	94%
2,3,5,6 - tetrafluorobenzenethiol	47.2	31.3	66%
2,3,4,5,6 - pentafluorobenzenethiol	51.9	28.7	55%

Figure 3. Results of QCM analysis of monolayer film formation.

4.3 Contact Angle Analysis

A relatively large contact angle hysteresis was observed on all SAMs (Figure 4). Chemical heterogeneity and deviation from the ideal well-ordered arrangement, in the case of fluorine substituted aromatic thiols, was demonstrated by a systematic increase in contact angle hysteresis with the number of fluorine substituents.

Thiol SAMs	θADVANCING (Degrees)	θRECEDING (Degrees)	θSTATIC (Degrees)	Δ θ (Degrees)
Allyl mercaptan	85 ± 3	37 ± 2	76 ± 3	48
3-chloro-1-propanethiol	83 ± 3	55 ± 2	82 ± 3	28
4-fluorophenylmethanethiol	85 ± 3	47 ± 3	70 ± 3	38
2,3,5,6 – tetrafluorobenzenethiol	85 ± 3	44 ± 2	74 ± 3	41
2,3,4,5,6 - pentafluorobenzenethiol	83 ± 5	40 ± 2	73 ± 3	43

Figure 4.

4.4 Surface Composition

X-ray photoelectron spectroscopy results revealed an anomalously large carbon to gold ratio for the surface composition of the allyl mercaptan SAM (Figure 5), consistent with the results obtained from QCM experiments. This can be attributed to allyl mercaptan's tendency to form multilayers. The unusually high ratio of C1s to F1s integrated intensities generated by 2, 3, 5, 6 - tetrafluorobenzethiol SAM suggests the coadsorption of adventitious hydrocarbons on the incomplete monolayer. In the case of 2,3,4,5,6 pentafluorobenzenethiol and 4-fluorophenylmethanethiol, the C1s to F1s ratios are in close agreement with the theoretical values.

Integrated Intensities	**Photoelectron Signals**					
	C_7H_7FS		$C_6H_2F_4S$		C_6HF_5S	
	C1s	F1s	C1s	F1s	C1s	F1s
% Atomic Concentration	49.58	7.25	43.24	14.36	53.76	16.17
Experimental Ratio of Atomic Concentration	6.8	1	3.0	1.0	3.3	1.0
Theoretical Ratio of Atomic Concentration	7.0	1	1.5	1.0	1.2	1.0

Figure 5.

4.5 Simultaneous Adhesion and Contact Current Measurements with AFM/STM

Vapor deposition with long-chain *n*-alkanethiols proved to be an inappropriate lubrication scheme for MEMS devices that require electrical contact. Results from preliminary investigation have shown that these molecules tend to form strong a dielectric barrier, and therefore they are considered poor candidates for lubrication of RF MEMS switches. On the other hand, measurements with vapor-deposited C_2SH SAMs produced some interesting results. It was observed that apart from a significant decrease in adhesion compared to its solvent-deposited counterpart, it also maintained current flow up to saturation coverage for an extend series of contact measurements (Figure 6).

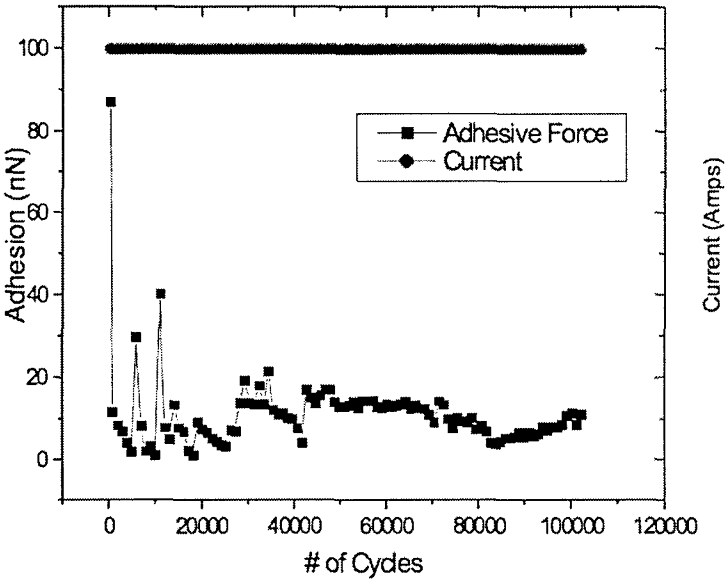


Figure 6. Simultaneous adhesion and current measurements performed with AFM under continuous flow of fluorinated thiol.

In an effort to lubricate gold contacts through a vapor phase approach, similar studies have been conducted in which the adsorption of fluorinated thiols has been explorted. Adsorption, adhesion, current flow measurements have been performed on a series of five different thiol molecules deposited from the vapor phase: Allyl mercaptan; 2,3,5,6-tetrafluorobenzenethiol; 2,3,4,5,6-pentafluorobenzenethiol; 3-chloropropane-1-thiol; and 4-fluorophenylmethanethiol. As reported in earlier sections, correlated results from QCM and contact angle measurements reveal that as the number of fluorine substituents increases, the self-assembled monolayers (SAMs) formed tend to be less ordered as evidenced by a systematic decrease in the percent saturation coverage and an increase in contact angle hysteresis. Interfacial adhesion with these SAMs and two different AFM tips have been measured statically using AFM and yielded a proportional decrease in adhesion as the number of fluorine substituents increases, regardless of the nature of the interface.

Adhesive force between vapor-deposited fluorinated SAMs and Si_3N_4 AFM tip and between fluorinated SAMs and Au-coated Si tip were measured statically using AFM. There was no tip damage or wear detected throughout the course of the experiment as there was no appreciable change in the radius of curvature within the range of the calculated standard deviation. The radius of curvature of the Si_3N_4 tip was characterized to be ~40±18 Å and ~38±15 Å prior to and after the measurements, respectively. Measurement results (Figure 7) revealed a proportional decrease in adhesion was observed as the number of fluorine substituents is increased. These results strongly indicate the compositional dependence of interfacial adhesion with the number of fluorine substituents.

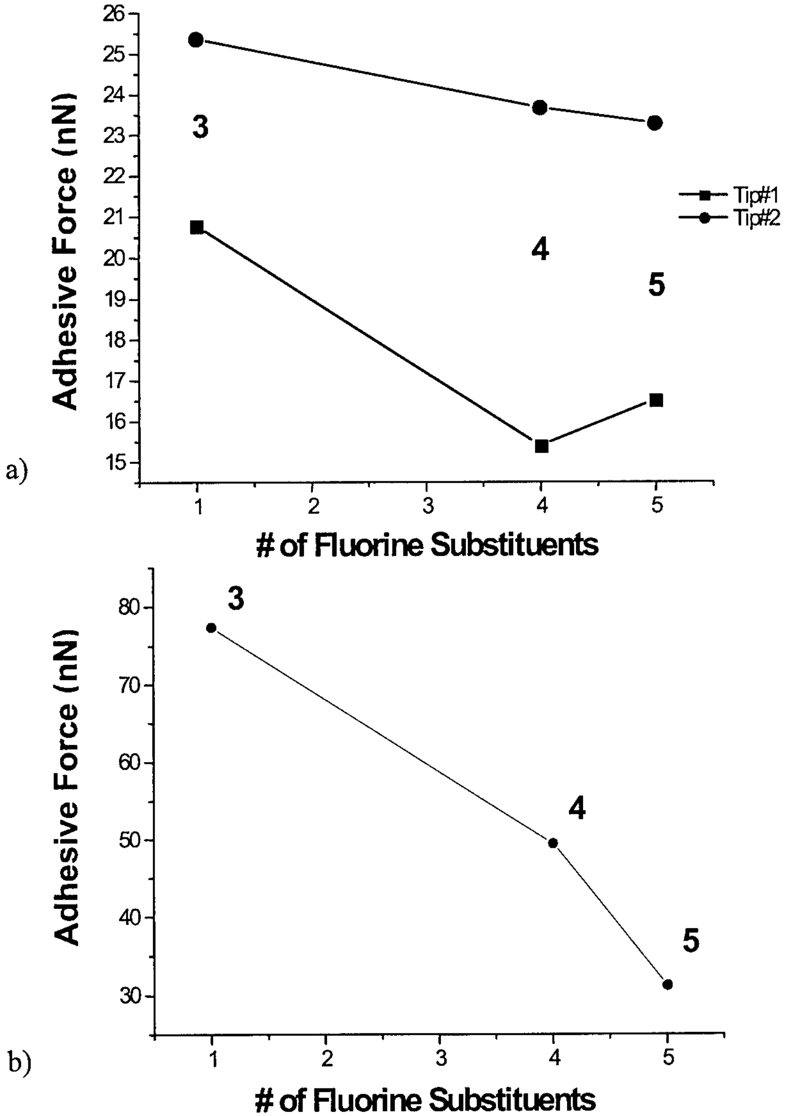
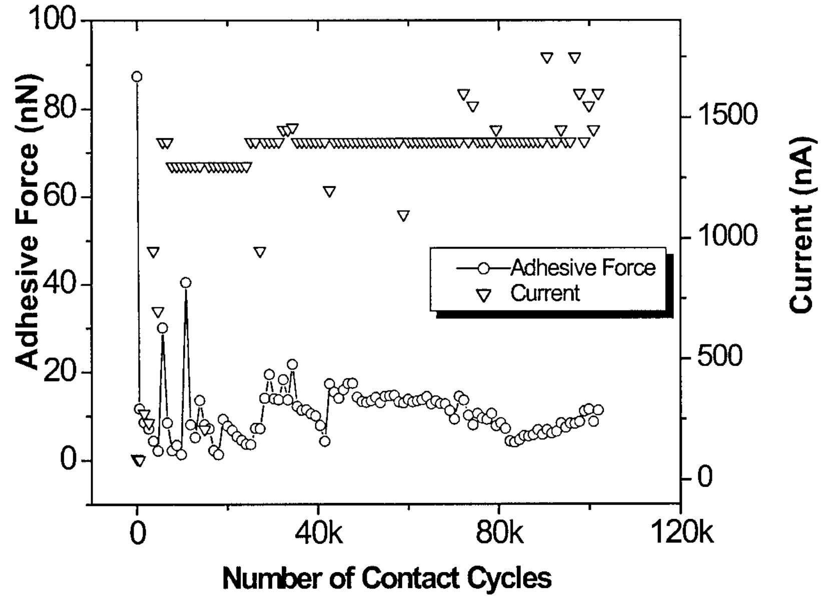


Figure 7. Interfacial adhesion measured between (a)aromatic thiol-SAMs and Si_3N_4 tip, and (b) between aromatic thiol-SAMs and Au-coated Si tip measured under static conditions.

On the other hand, the radius of curvature of the Au-coated silicon AFM tip was characterized to be ~115±34 Å and ~117±31 Å prior to and after the measurements, respectively. Again, this indicates that the tip did not suffer any significant wear or damage throughout the course of the experiment, which could otherwise severely affect the adhesion results. Results revealed a proportional decrease in adhesion was observed as the number of fluorine substituents is increased, similar to the trend observed between Si_3N_4 AFM tip and fluorinated aromatic SAMs. Overall results demonstrate that lower adhesion can be achieved by increasing the number of fluorine substituents regardless of the nature of the interacting substrates, in a similar manner when increasing the hydrocarbon the chain length.

Direct and real-time monitoring of the adhesion and current flow at the points of intermittent contact (1Hz) under a flow of vapor phase thiol molecules on a clean Au substrate yielded the results presented in Figure 8. C_7H_7FS was chosen as an exemplary molecule since it forms a more ordered film compared to the other two aromatic thiol molecules. The graph in shows a significant decrease in adhesion was achieved while current was sustained between the two metal electrodes for well over 100,000 tip-sample contact cycles. There was no tip damage or wear detected throughout the course of the experiment as there was no appreciable change in the radius of curvature within the range of the calculated standard deviation. The radius of curvature of the Au-coated AFM tip was characterized to be ~115±34 Å and ~118±46 Å prior to and after the measurements, respectively. Results have shown that SAMs with fluorine moieties heavily influence the tribological properties of two interacting metal surfaces by preventing wear for over a hundred thousand contact cycles as well as significant reduction in adhesion, while sustaining current flow under the conditions of modest bias setting. The correlated contact pressures, current densities and adhesive forces as a function of number of contact cycles are presented in Figure 8. Based on JKR (Johnson-Kendall-Roberts approximation, the contact areas and the corresponding contact pressures have been calculated. As shown, the current density did not change appreciably for a fairly constant contact pressure throughout the several thousand cycles of intermittent contacts, except for some minor spurious response in between. This clearly demonstrates that through fine structural control of the surface composition between conducting and contacting surfaces, successful lubrication can be achieved without compromising electrical conductivity throughout several thousand contact cycles a)



b)

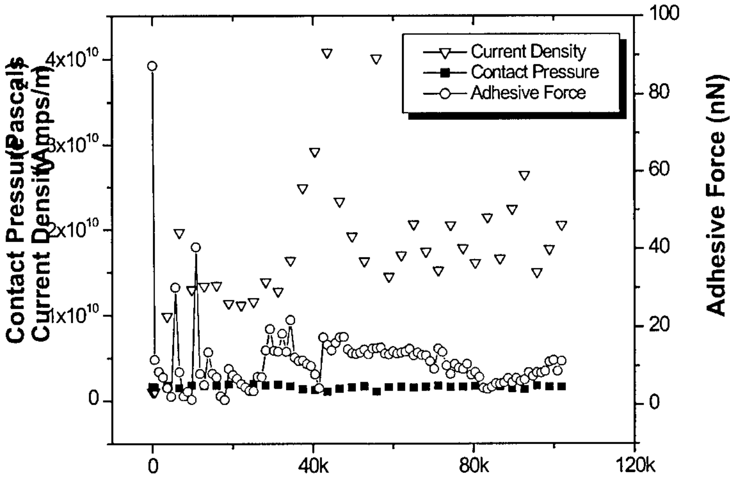


Figure 8. Current flow and adhesion measured with a 0.30 V bias between a gold-coated AFM tip and a gold substrate as a function of the duration of flow of vapors of C_7H_7FS. The graph shows a significant decrease in adhesion was achieved while current was sustained between the two metal electrodes for over 100,000 switching cycles.

4. 6 Summary

In this study, the vapor phase lubrication of interacting gold surfaces has been investigated on the atomic and molecular level using the quartz crystal microbalance (QCM), atomic force microscopy (AFM) and scanning tunneling microscopy (STM). These techniques have provided a fundamental understanding of the molecular nature of adsorption, adhesion, and current flow occurring at gold interfaces through the formation of self-assembled monolayers of conjugated aromatic thiol molecules. The issues of static adhesion and contact performance have been addressed simultaneously in relation to the nature and composition of the interface. Maps of both current and adhesion demonstrated the potential of using conjugated species with fluorine substituents on the basis of their tribological and electrical behavior as candidates for lubricating Au/Au interfaces in MEMS devices. Although they do not form a closely-packed geometry compared to *n*-alkanethiol SAMs, they however provide hydrophobic,"Teflon-like" surfaces which accounts for the observed low adhesion. However, further studies must be done to investigate the reliability of this system for an extended period of time and explore the chemistry that is going on in the interface after millions or even billions of contact cycles.

5. Personnel Supported

University of Houston

Mr. Gang Liang, Graduate student, 100%
Mr. Ian Laboriente, Graduate student, 100%
Dr. Scott S. Perry, Associate Professor, 8.3% (1 month summer)

6. Publications and Presentations

Publications

- Shuang Li, Paul Cao, Ramon Colorado, Jr., Irmgard Wenzl, Olga E. Shmakova, Michael Graupe, T. Randall Lee and Scott S. Perry, *Local Packing within the Outermost Atomic Layer Strongly Influences the Friction of Mixed CH_3- and CF_3-Terminated Alkanethiol SAMs on Au(111)* Langmuir, **21**(3), (2005) 993.

- Scott S. Perry, Wilfred T. Tysoe, "*Frontiers of Fundamental Tribological Research,* Tribology Letters, **19**(3) (2005) 151.

Presentations

- Gang Liang and Scott S. Perry, " Frictional Properties of the Lubricants and Coatings for Micro-Electromechanical Systems Studied by Atomic Force Microscopy", Physical Chemistry Division Seminar, Department of Chemistry, University of Houston

7. Interactions/Transitions

Prof. Scott Perry continues to play a leading role in the tribological community focused on fundamental measurements at the atomic and molecular scale. His role in conference and workshop organization demonstrates the service to the community in this area.

Prof. Scott S. Perry
Organizer
NSF-sponsored workshop "Frontiers of Tribological Research"
October 6-8, 2004
Houston, TX

Prof. Scott S. Perry
Co-Organizer
ACS National Symposim on Tribology
San Diego, CA
March, 2006

8. New discoveries, inventions, or patent disclosures.

9. Honors/Awards:

Scott S. Perry

Phi Beta Kappa National Honor Society, Furman University, Alumni Inductee	2005
Phi Kappa Psi National Honor Society, University of Houston, Faculty Inductee	2005