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   Nanotribology Investigations of Solid and Liquid Lubricants
   Using Scanning Probe Microscopies

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13. ABSTRACT (Maximum 200 Words)
   To understand and control friction and wear in both macroscopic and microscopic technologies requires a detailed understanding of material properties, chemical reactivity and intermolecular interactions on the nanometer length scale. The role of nanoscale defects on friction has been elucidated through scanning tunneling microscopy and atomic force microscopy studies of molybdenum disulfide. These investigations have shown that friction increases systematically with increasing defect density, and have demonstrated a novel load-independent friction regime due to sliding on constant area nanocrystals. The mechanical properties of finite size materials, which are important to micro and nanomechanical systems, have also been probed through studies of the bending of different thickness molybdenum oxide nanocrystals. Significantly, this work has shown that there is a substantial and systematic decrease in the modulus with decreasing thickness. This large drop in stiffness shows that materials will exhibit greater flexibility as their dimensions are reduced. Lastly, a new generation of molecular resolution tools has been developed. Carbon nanotubes were attached to conventional force microscopy tips and shown to provide large improvements in image resolution. Methods to localize molecules at the nanotube ends were also developed, and these modified probes were used to measure intermolecular forces and image with chemical sensitivity.

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Abstract.

To understand and control friction and wear in both macroscopic and microscopic technologies requires a detailed understanding of material properties, chemical reactivity and intermolecular interactions on the nanometer length scale. The role of nanoscale defects on friction has been elucidated through scanning tunneling microscopy and atomic force microscopy studies of molybdenum disulfide. These investigations have shown that friction increases systematically with increasing defect density, and have demonstrated a novel load-independent friction regime due to sliding on constant area nanocrystals. The mechanical properties of finite size materials, which are important to micro and nanomechanical systems, have also been probed through studies of the bending of different thickness molybdenum oxide nanocrystals. Significantly, this work has shown that there is a substantial and systematic decrease in the modulus with decreasing thickness. This large drop in stiffness shows that materials will exhibit greater flexibility as their dimensions are reduced. Lastly, a new generation of molecular resolution tools has been developed. Carbon nanotubes were attached to conventional force microscopy tips and shown to provide large improvements in image resolution. Methods to localize molecules at the nanotube ends were also developed, and these modified probes were used to measure intermolecular forces and image with chemical sensitivity.
I. Introduction.

To understand and control friction and wear in both macroscopic and microscopic technologies requires a detailed understanding of material properties, chemical reactivity and intermolecular interactions on the nanometer length scale. This report describes the results of studies carried out over the past three years that have addressed these critical issues. In particular, three main areas have been at the focus of this project; these are: (1) nanometer scale studies of defects and friction using atomic force and scanning tunneling microscopies; (2) nanometer scale studies of the mechanical properties of finite size materials using atomic force microscopy; and (3) development of molecular resolution and chemically sensitive scanning probe microscopy tips. The investigations and resulting data from these three areas are described in sequence below.

II. Nanotribology: Controlled Studies of Defects & Friction.

Macroscopic studies of friction, lubrication and wear have contributed much to the phenomenological understanding of tribology. Studies of the interactions between macroscopic bodies are influenced by complex factors that can be disentangled through nanometer measurements of friction and intermolecular forces. Such microscopic information is also of importance to many areas of nanoscale science and technology, including the manipulation and assembly of nanostructures and microelectromechanical systems (MEMS).

To address how defects on surfaces influence friction, we have systematically created, characterized and studied defects on MoS$_2$ single crystal surfaces in ultrahigh vacuum (UHV) using STM and AFM instrumentation set-up under the prior AFOSR award. The defects were created on MoS$_2$ surfaces by thermal oxidation, and are thus also relevant to the degradation of this model lubricant system.

UHV STM studies of freshly cleaved and thermally oxidized MoS$_2$ single crystal surfaces (Fig. 1) have been used to characterize several distinct types of defects. Circular, 4-5 nm features, which appear dark at both positive and negative bias, are observed on freshly cleaved MoS$_2$ (no.1, Fig. 1a) and oxidized MoS$_2$. Previous studies have shown that these defects can be associated with metal impurities in the crystal (Ti and V), and indeed, we find that the defect density agrees well with the measured impurity concentration. Thermal oxidation produces

![Figure 1](image)

Figure 1. Ultrahigh vacuum STM characterization of defects on oxidized MoS$_2$ single crystals. The images correspond to (a) freshly cleaved MoS$_2$, (b) MoS$_2$ oxidized for five minutes at 470 °C and (c) MoS$_2$ oxidized for seven minutes at 470 °C. The bright features in (c) correspond to 2-4 nm MoO$_3$ nanocrystals. (d) Atomic-resolution view of the one nanocrystal from sample shown in (c). The images are 20nm x 20nm (a-c) and 8 nm x 8 nm (d).

two new types of defects: atomic-scale surface pits (no.2, Fig. 1b) and larger raised structures 2-4 nm in diameter (no.3, Fig. 1c). The densities of these defects were found to increase with increasing oxidation time. Significantly, the 2-4 nm structures can be moved by the STM tip.
Based on our previous studies of MoO₃ nanocrystal manipulation and XPS studies, which show the presence of MoO₃ on surfaces oxidized for seven minutes, we can attribute the 2-4 nm structures to very small MoO₃ nanocrystals.

To investigate how these defects affect friction, we have used UHV AFM to characterize the same samples studied by STM without removal from the vacuum system (Fig. 2). In general, we find that the lateral friction force increases linearly with load for the freshly cleaved MoS₂ and MoS₂ sample oxidized for 5-minutes. Moreover, the friction on this oxidized sample is 2-3 times larger than the clean surface for the same loads. Based on the STM results, we can conclude that the friction force--dissipation--increases in the presence of the small pits that nucleate the growth of MoO₃. It is likely that the enhanced dissipation arises from the greater tip-sample interaction at these nucleation sites due to dangling bonds, etc. It is not possible using currently available Si₃N₄ or Si probes to investigate this in greater detail at the single defect level.

**Figure 2.** Ultrahigh vacuum AFM measurements of friction vs load on oxidized MoS₂ single crystals. (a) Friction vs load obtained with Si₃N₄ tips on freshly cleaved MoS₂ (squares/blue line), MoS₂ oxidized for five minutes at 470 °C (circles/red line) and MoS₂ oxidized for seven minutes at 470 °C (triangles/green line). The latter friction data is independent of load. (b) Data recorded on MoS₂ oxidized for 7 minutes. (red) Initial results obtained with a clean tip starting at low load and increasing. (green) curves obtained at different sample locations and with different cantilever/tip assemblies.

For oxidation times greater than five minutes, we observe the presence of very small 2-4 nm MoO₃ nanocrystals (Fig. 1c). Qualitatively, one would expect these larger defects to further increase dissipation and friction in the sliding contacts. This is indeed true for loads less than ca. 10 nN. However, we also find totally unexpected behavior on these samples; that is, the friction is independent of load. Hence, at higher loads the total friction on the seven minute oxidized sample becomes less than that on samples containing fewer defects. We find that the load-independent friction observed on these samples is very reproducible and robust (e.g., Fig. 2b): we observe similar behavior and friction forces for Si₃N₄, Au-coated Si₃N₄, Ti-coated Si₃N₄, and Si tips. When using a tip for the first time, however, we often observe an initial linear increase in friction at lower loads followed by a sudden drop to load-independent friction (Fig. 2b).

We have been able to explain consistently these novel results with a model where the tip-surface contact is mediated by a MoO₃ nanocrystal. When the probe tip is scanned on the oxidized MoS₂ surface, a MoO₃ nanocrystal can adhere to the tip apex. This produces a space between the tip and substrate whereby the contact interface is an atomically-defined area that does not change with increasing load. It is this fixed area contact that gives rise to the new load-
independent behavior. We believe that these results suggest an interesting approach to the design of improved lubricants that exploits nano load-bearing particles. This approach could be especially attractive for making well-defined and robust contacts in MEMS and other nanometer/micron-scale mechanical devices.

III. Mechanical Properties of Nanoscale Materials.

The mechanical properties of nanometer scale structures are of considerable interest to both fundamental science and technology. The mechanical properties of finite size materials might change significantly relative to bulk values due, for example, to the increasing ratio of under-coordinated surface to bulk atoms as structures are made smaller and smaller. However, such size-dependent effects have been difficult to characterize experimentally. This nanometer size regime is also theoretically challenging, because it falls between those treated conventionally using atomistic and continuum models. Moreover, a fundamental understanding of mechanical properties at the nanoscale is essential to applications ranging from micro- and nanoscale mechanical systems to nanostructured composites.

We have exploited AFM to address this fundamentally and technologically important issue through studies of the bending of different thickness MoO$_3$ nanocrystal plates. We chose the MoO$_3$/MoS$_2$ system, which had been developed previously in our laboratory through AFOSR-funded studies, since (1) MoO$_3$ nanoplates of varying thickness can be rationally grown by thermal oxidation of MoS$_2$, (2) the resulting MoO$_3$ structures can be manipulated with an AFM over step edges to create freely suspended ends, and (3) the force vs deflection of these suspended nanoplate ends can be conveniently measured with the AFM to assess the modulus for a given thickness. A schematic illustrating our new experimental concept and an experimentally observed MoO$_3$ nanocrystal overhanging a large step on the MoS$_2$ surface are shown in Figure 3.

![Figure 3.](image)

Figure 3. (A) Schematic of the experimental approach used to probe the mechanical properties of the MoO$_3$ nanoplates. The geometry is characterized by imaging at low loads (without plate deflection). (B) Typical AFM image of MoO$_3$ nanocrystals on a MoS$_2$ substrate near a step.

After creating suspended nanoplate structures like Figure 3b, we measured the normal force vs displacement on a grid of points encompassing both the overhanging portion of the MoO$_3$ nanoplate and the portion suspended by the MoS$_2$ substrate. For each point on the force-displacement matrix we calculate the slope; this slope is related to the Young's modulus $E$ by a
geometrical factor. Qualitatively, we found that the slopes were constant over the MoS$_2$ region and decreased as the distance from the step edge increases (on the suspended portion). These observations agree qualitatively with expectations.

To calculate quantitatively $E$, we took into account the exact geometry of the each MoO$_3$ nanoplate by using Finite Element Analysis. A summary of our results from this type of analysis carried out on crystals of varying thickness is shown in Figure 4. Significantly, we have

**Figure 4.** Plot of the Young's modulus, $E$, versus nanocrystal thickness. The unit cell thickness of MoO$_3$ is ca. 1.5 nm, and thus these measurements span crystals with thicknesses from 3-10 unit cells.

found that there is a substantial and systematic decrease in the Young's modulus with decreasing nanocrystal thickness. This large drop in $E$ has important implications for potential applications: specifically, it shows that materials will exhibit much greater flexibility as their dimensions are reduced. We have demonstrated this latter point in studies of 1 and 2 unit cell thick crystals that move conformally over steps and other surface perturbations.

**IV. Carbon Nanotube Probe Microscopy Tips.**

We have also initiated and made substantial progress on a new area-- the development of carbon nanotube AFM tips. These tips represents ideal probes for investigating phenomena at nanometer scale, and offer the opportunity for revolutionizing many areas of science and technology.

**Fabrication and imaging with carbon nanotube tips.** The preparation and characterization of carbon nanotube tips is now well-established in the P.I.'s laboratory. SWNT and MWNT bundles are attached to the pyramids of gold-coated Si cantilevers using an acrylic adhesive under the direct view (500-1000 x; dark field illumination) of an optical microscope using 3-axis micromanipulators (Fig. 5). This bundle structure has several important implications.
First, the bundle structure is important for creating a tip that is sufficiently rigid so that thermally-excited vibrations do not degrade the image resolution when the length is on the order of a micron or less. A less positive attribute is that the overall length and diameter of mounted bundles require that they be shortened and sharpened for high-resolution imaging.

We have investigated the lateral resolution of MWNT and SWNT bundle tips by imaging inorganic (Au nanoclusters) and biological (e.g., DNA) standards. The tip radii are determined quantitatively from observed image widths and known sizes of the standards. These initial data, which are summarized in Table 1, show the great promise of nanotubes and especially SWNTs as ultrahigh resolution AFM tips. For example, in several cases we have been able to observe radii of ca 3 nm for tips prepared from SWNT bundles, and these radii are significantly better than the \( \bullet 10 \) nm we generally observe with Si or Si\(_n\)N\(_x\) tips. However, it is also important to note these best values cannot be obtained reproducibly: the typical radii for MWNT and SWNT bundle tips are 8-12 and 5-10 nm, respectively. Moreover, even the best values observed are far larger than the 0.5 nm possible with a single SWNT tip.
### TABLE 1. Comparison of the resolution of Si, MWNT, and SWNT tips.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tip</th>
<th>Apparent Full Width at Half-Max. (in nm)</th>
<th>Calculated tip radius of curvature (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>type-1 amyloid fibril</td>
<td>Etched Si FESP</td>
<td>21.5 ± 1.8</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>MWNT</td>
<td>18.6 ± 2.2</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>SWNT</td>
<td>11.9 ± 0.7</td>
<td>2.6</td>
</tr>
<tr>
<td>5 nm diameter Au colloid</td>
<td>Etched Si FESP</td>
<td>17.2 ± 2.0</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>MWNT</td>
<td>13.0 ± 2.1</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>SWNT</td>
<td>10.6 ± 2.6</td>
<td>3.4</td>
</tr>
<tr>
<td>lambda DNA</td>
<td>Etched Si FESP</td>
<td>15 ± 3</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>SWNT</td>
<td>5 ± 1</td>
<td>3</td>
</tr>
</tbody>
</table>

**Direct Growth of Nanotube Tips.** The attached bundle tips described above do have limitations, including (i) the mounting procedure inherently selects against smaller and potentially sharper bundles since these are more difficult to observe while mounting and (ii) a relatively long time is required to attach bundles. To overcome these limitations we have investigated the direct growth of individual carbon nanotubes from the ends of Si tips by chemical vapor deposition (CVD), since this method could produce tips that would not need sharpening (they already are single tubes), and moreover, this approach could be carried out on a larger scale to make the tips widely accessible.

A schematic of the approach used for the direct CVD growth of nanotubes is illustrated in Figure 6. A conventional Si tip, which has been flattened at its apex, is anisotropically etched to

**Figure 6.** Growth of oriented carbon nanotube tips. The end of the tip of a conventional silicon cantilever is anisotropically-etched of ion-milled to create nanoscale pores perpendicular to the plane of the cantilever beam. Catalyst is deposited into the pore bottoms, and then oriented nanotubes are grown by CVD.
create nanopores along the tip axis. Alternatively, focused ion milling could be used to create nanopores at well-defined locations on the tip-apex. An oriented pore structure has been chosen for the catalyst support in order to control the growth direction and enable the reproducible production of nanotube tips for imaging. Previous studies of bulk nanotube growth have demonstrated that nanotubes produced by CVD grow aligned with the pore direction when using mesoporous structures for the catalyst support. After the pore structure is formed, catalyst is deposited into the pores, and then nanotubes are grown from the catalyst particles by CVD using a hydrocarbon gas.

Significantly, our preliminary studies show that well-defined CVD nanotube tips can be reproducibly formed after several minutes of CVD growth at 750 °C using ethylene (Fig. 7). A high-resolution FE-SEM image shows a well-defined 480 nm long tube protruding from the Si

![Figure 7](image_url)

**Figure 7.** Characterization of CVD nanotubes tips. (left) FE-SEM image of a CVD nanotube tip that has been shortened for imaging. (right) TEM image of a CVD nanotube tip. The entire AFM cantilever/tip assembly with nanotube tip was mounted on a custom TEM holder for imaging. The scale bar is 100 nm.

tip apex. A second 100 nm nanotube is also observed but is sufficiently short that it does not interfere with the primary tip. Higher resolution FE-SEM images of a number of nanotube tips produced under these conditions show that the average diameter is $10 \pm 5$ nm. TEM images (Fig. 7) show that the tips grown under these conditions are MWNTs with well-ordered graphene planes. In addition, AFM measurements of the cantilever oscillation amplitude vs position above a substrate surface have been used to characterize the mechanical properties of the CVD nanotube tips. These experiments show the characteristic elastic buckling of the nanotube structure.

We have characterized the imaging performance of the CVD nanotube probes using colloidal gold nanoparticle standards, which are a relatively incompressible materials with well-defined diameters. Our preliminary data are summarized in Table-2. In general, the results show that we obtain very high-resolution tips with end radii between 3 nm and 6 nm.
Table 2. Summary of CVD nanotube tip resolution data.

<table>
<thead>
<tr>
<th>Tip No.</th>
<th>01C</th>
<th>20E</th>
<th>38A</th>
<th>31G</th>
<th>38B*</th>
</tr>
</thead>
<tbody>
<tr>
<td>radius ± 1σ (nm)</td>
<td>3.7 ± 0.7</td>
<td>4.4 ± 0.5</td>
<td>5.7 ± 1.7</td>
<td>3.2 ± 0.7</td>
<td>5.3 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.5 ± 0.7</td>
</tr>
</tbody>
</table>

The tips are defined by a specific number and a capital letter. The number designates a particular tip and the letter the growth cycle, where A=1. The resolution was calculated using a two-sphere model using the full-width at half-maximum determined from the experimental images. The upper and lower values correspond to results obtained from 5 and 2 nm gold nanoparticles, respectively.

These results represent a significant improvement over the best MWNT bundle tips that we have prepared in the past and commercial Si tips, although are still larger than the limit of a single SWNT. We have also found that the Si cantilever/tip assemblies can be reused several times to grow new nanotube tips. When a tip ultimately fails, all carbon is removed by oxidation (500 °C), and then a new tip is grown by CVD. For example, tip 31G (the letter designates the number of growth/oxidation cycles with A=1) exhibits excellent resolution after 6 repeat growths, and the 38A and 38B tips produced in sequential runs are comparable.

Chemical functionalization of carbon nanotube probe tips. We have also made significant progress in our studies exploring the functionalization of carbon nanotube tips for the purpose of chemically sensitive imaging. Open-ended nanotube tips are formed while shortening the tubes in an oxidizing environment prior to use. We have characterized these open ends in MWNT and SWNT using transmission electron microscopy (TEM) as shown in Figure 8. Carboxyl groups are expected at open ends on the basis of previous spectroscopic studies of oxidized bulk nanotube and graphite samples.

![Figure 8. TEM image showing the open end of a shortened MWNT tip.](image)

To demonstrate the presence of carboxyl groups at the tip ends, we have measured the adhesion force vs pH between tips and a planar substrates modified with self-assembled monolayers (SAMs) terminating in hydroxyl groups. This procedure enables us to effective titrate ionizable acidic and basic groups on the tip end (termed a force titration). Significantly, force titrations recorded between pH 2 and 9 with MWNT and SWNT tips on hydroxyl-terminated
monolayers exhibit well-defined drops in the adhesion force at ca. pH 4.5 that are characteristic of the deprotonation of a carboxylic acid (Fig. 9). The observation of carboxyl groups at the nanotube tip ends provides a handle for chemically-sensitive imaging, and moreover, these carboxyl groups can be further elaborated to create nanotube probes that are sensitive to a wide range of functionality.

![Figure 9](image)

**Figure 9.** Adhesion force as a function of pH between a MWNT tip and a hydroxyl-terminated SAM (11-thioundecanol on gold-coated mica). Each data point corresponds to the mean of 50 - 100 adhesion measurements, and the error bars represent one standard deviation.

Specifically, our preliminary studies have shown that the carboxyl group can be derivatized by coupling with amines (Fig. 10). The success of this coupling chemistry was

![Figure 10](image)

**Figure 10.** Schematic representation of the chemical functionalization of a carbon nanotube end with an amine, using EDC (1-Ethyl-3-(dimethylaminopropyl) carbodiimide).

demonstrated by force titrations. Nanotube tips modified with benzylamine, which exposes nonionizable, hydrophobic functional groups at the tip end, yielded pH-independent interaction force on hydroxyl-terminated monolayers. This covalent modification thus eliminates the prominent pH-dependent behavior observed with the unfunctionalized tips. Moreover, force titrations with ethylenediamine modified tips exhibit no adhesion at low pH and finite adhesion above pH 7. These pH-dependent interactions are consistent with our expectations for an exposed basic amine functionality that is protonated and charged at low pH and neutral at high pH.
**Reactive Gas Functionalization.** A new and promising approach for the functionalization of the nanotube probes prepared in our studies involves direct modification in a reactive gas during sharpening and/or shortening procedures. The motivation for these studies are that a direct process could (i) prepare tips with different functionality more efficiently than at present and (ii) this process could be used to prepare modified tips *in-situ* for UHV studies.

The idea underlying our proposed approach is outlined schematically in Figure 11. In the case of the carboxyl (-COOH) groups that we have shown to be present at the tips ends, the our

![Figure 11. Schematic of carbon nanotube functionalization process.](image)

(a) Carbon nanotube (heavy, black vertical line) attached to a Si cantilever is oscillated near resonance above a sputtered Nb surface in the presence of gas, X2. (b) A potential applied between the oscillating cantilever/nanotube assembly and sputtered Nb substrate produces a discharge that activates surrounding gas molecules (X2+, X2*). (c) Subsequent reaction at the nanotube tip produces a tip functionalized with ‘X’. In these studies, X corresponds to O, H, or N.

The proposed mechanism is as follows. The potential applied between the oscillating cantilever/nanotube tip and metal (Nb) surface produces a momentary arc discharge. In this discharge, two things occur. First, carbon is removed from the nanotube end in a process believed to be assisted by high electric fields. This process creates reactive carbon sites at the tube end. Second, the discharge can activate, through field and electron impact ionization, the surrounding gas molecules. In the cases of H2, N2, and O2, ionized (e.g., H2+, N2+, and O2+, respectively), excited state and atomic species can be produced. We have proposed that it is activated oxygen that reacts at nanotube ends to form the observed carboxyl groups.
Significantly, our studies of nanotube functionalization in H₂, N₂, and H₂/N₂ mixtures demonstrate the promise of this new approach. Force titrations recorded on MWNT tips modified in N₂ exhibit pH-dependent behavior with no measurable force at low pH and finite adhesion at pH > 8 (Fig. 12). This pH dependent behavior shows that MWNT tips modified in N₂ have basic functionality at their ends. In addition, force titrations carried out on tips modified in H₂ show pH independent adhesion, and thus demonstrate that nonioziable/hydrophobic ends can also be created.

**Chemical mapping with modified nanotube probe tips.** Our studies have also shown that the modified nanotube probes can be used for chemically sensitive imaging. Previously, we showed that it was possible to exploit specific functionalization of commercial probe tips with organic monolayers to discriminate chemically specific forces and thereby image heterogeneous organic layers with chemical sensitivity. Such functional group sensitive imaging, which is called chemical force microscopy (CFM), was initially carried out in contact mode by recording chemically specific differences in friction. More recently, we have shown chemical mapping also can be carried out in the intermittent contact or tapping mode. In the regime of light tapping, we have found that phase-lag between chemically distinct surface regions is directly related to the difference in intermolecular interactions (or adhesion):

\[
\Delta \Phi \frac{k}{Q} \propto \Delta W_{st}
\]

where \(\Delta \Phi\) is the change in phase lag, \(k\) is the spring constant, \(Q\) is the cantilever quality factor and \(\Delta W_{st}\) is the difference between the work of adhesion for the tip interacting with chemically-distinct sample regions. These new results now provide another flexible method for chemical mapping of surface that is especially attractive for nanotube tips.
Significantly, we have used functionalized nanotube probes to obtain high-resolution, chemically sensitive images of patterned monolayer and bilayer samples in tapping mode (Fig. 13). Tapping mode images recorded with -COOH and benzyl terminated tips exhibit greater

**Figure 12.** Chemically sensitive imaging with functionalized nanotube tips. (a) Schematic of a patterned sample consisting of 10 μm squares of a methyl-terminated (hexadecanethiol) monolayer region surrounded by a carboxylic acid-terminated (16-mercaptohexadecanoic acid) monolayer background on gold. Tapping mode phase lag images of the patterned sample in ethanol recorded with (b) an unmodified nanotube tip (COOH terminated) and (c) a benzylamine functionalized nanotube tip (phenyl terminated). Darker regions indicate greater phase lag.

phase lag on the -COOH and -CH₃ sample regions, respectively, and these results are consistent with expected and measured intermolecular forces between the functionalized tips and monolayer patterned sample. In addition, analysis of results obtained with one SWNT bundle tip on a chemically-heterogeneous bilayer sample showed a chemical resolution of 3-4 nm. This resolution is ca. 5x better than with previous tips and represents a clear proof-of-concept for our proposed ultrahigh resolution mapping studies discussed below.
V. PUBLICATIONS SUPPORTED BY AFOSR


VI. PERSONNEL SUPPORTED.

1. Aleksandr Noy, graduate student
2. Dmitri Vezhenov, graduate student
3. JinLin Huang, research associate
4. Jianfang Wang, graduate student (partial support)
5. Latha Venkataraman, graduate student (partial support)
6. Kai Rose, postdoctoral fellow (external fellowship support; supplies on AFOSR)
7. Ernesto Joselevich, postdoctoral fellow (external fellowship support; supplies on AFOSR)
8. Teri Wang Odom, graduate student, partial support
9. Yi Cui, graduate student
VII. INTERACTIONS/TRANSITIONS

A. PRESENTATIONS AT MEETINGS, CONFERENCES AND SEMINARS.


17


40. "Chemistry and Physics in One-Dimension: Synthesis, Properties and Applications of Nanowires and Nanotubes", Purdue University, West Lafayette, IN, November 12, 1998.


42. "Advances in Force Microscopy and Spectroscopy, with Bioprobes” workshop, University of Linz, Austria, January 31, 1999.


48. "Covalently Modified Nanotubes to Probe Biological Systems at the Nanometre Scale", Fourth Annual Microdevices for Biomedical Applications, Cambridge Healthtech Institute, San Jose, CA, April 20, 1999.


57. “Functionalized Carbon Nanotubes for Probing Chemical and Biological Systems at the Nanometer Scale”, Boston College Dept. of Chemistry 1999 Fall Seminar Series, Boston, MA, September 27, 1999.


B. CONSULTATIVE AND ADVISORY FUNCTIONS.

4. Member, Editorial Advisory Board, Chemistry of Materials (1997)
7. Member, Editorial Advisory Board, Accounts of Chemical Research (1992)

21
C. TRANSITIONS.

1. Nanotribology of MoS₂/MoO₃ Solid Lubricant System. Dr. Michael N. Gardos, Hughes Aircraft Company, 2000 E. El Segundo Boulevard, El Segundo, CA 90245; (310) 616-9890. Fundamental understanding of tribology at nanometer scale developed in P.I.s AFOSR studies are being used in further development of space-based lubricant systems. In addition, discussions have been initiated on application of AFOSR funded work to Hughes’ effort in MEMS and electrical contact lubricants.

D. EXTERNAL REPORTS ON AFOSR PUBLICATIONS/PRESENTATIONS


VIII. NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES


