



AFRL-AFOSR-JP-TR-2016-0053

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**Understanding the Atomic Scale Mechanism that controls the attainment of ultralow friction and wear in carbon based materials**

**Robert Carpick  
TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA**

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**05/16/2016  
Final Report**

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**Air Force Research Laboratory  
AF Office Of Scientific Research (AFOSR)/ IOA  
Arlington, Virginia 22203  
Air Force Materiel Command**

| <b>REPORT DOCUMENTATION PAGE</b>  |                    |                                |                                   | <i>Form Approved</i><br>OMB No. 0704-0188                         |   |
|---|--------------------|--------------------------------|-----------------------------------|---|---|
| <p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p><b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</b></p>  |                    |                                |                                   |   |   |
| <b>1. REPORT DATE (DD-MM-YYYY)</b><br>16-05-2016  |                    | <b>2. REPORT TYPE</b><br>Final |                                   | <b>3. DATES COVERED (From - To)</b><br>17 Jun 2014 to 16 Dec 2015 |   |
| <b>4. TITLE AND SUBTITLE</b><br>Understanding the Atomic Scale Mechanism that controls the attainment of ultralow friction and wear in carbon based materials   |                    |                                |                                   | <b>5a. CONTRACT NUMBER</b><br>FA2386-14-1-4071                    |   |
|   |                    |                                |                                   | <b>5b. GRANT NUMBER</b><br>Grant 14IOA087_144071                  |   |
|   |                    |                                |                                   | <b>5c. PROGRAM ELEMENT NUMBER</b><br>61102F                       |   |
| <b>6. AUTHOR(S)</b><br>Robert Carpick   |                    |                                |                                   | <b>5d. PROJECT NUMBER</b>   |   |
|   |                    |                                |                                   | <b>5e. TASK NUMBER</b>  |   |
|   |                    |                                |                                   | <b>5f. WORK UNIT NUMBER</b>                                       |   |
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br>TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA<br>3451 WALNUT ST<br>PHILADELPHIA, PA 19107-6205 US   |                    |                                |                                   | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b><br><br>N/A        |   |
| <b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b><br>AOARD<br>UNIT 45002<br>APO AP 96338-5002  |                    |                                |                                   | <b>10. SPONSOR/MONITOR'S ACRONYM(S)</b><br>AFRL/AFOSR/IOA(AOARD)  |   |
|   |                    |                                |                                   | <b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b><br>14IOA087_144071  |   |
| <b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b><br>Distribution Code A: Approved for public release, distribution is unlimited.  |                    |                                |                                   |   |   |
| <b>13. SUPPLEMENTARY NOTES</b>  |                    |                                |                                   |   |   |
| <b>14. ABSTRACT</b><br>The wear behavior of ultrananocrystalline diamond (UNCD) was characterized at the nanoscale to understand the fundamental mechanisms controlling the initial stages of wear. To enable this, novel nanoscale sliding experiments were conducted in situ in a transmission electron microscope (TEM). UNCD is part of a class of materials with tremendous potential for tribological applications due to their low wear and low friction behavior. However, the scientific understanding of the initial wear process is lacking, and this prevents broader application of these materials. The experiments revealed that: (1) the wear follows a gradual, atomic-level removal mechanism, as opposed to fracture or plastic deformation; (2) the rate of wear (rate of material removal) in this nanoscale, single asperity contact is orders of magnitude larger than that measured at the macroscale; and (3) nevertheless, the wear follows the macroscale trend of an initially larger wear rate, followed by stabilization at a lower value. Strikingly, no amorphization during sliding was observed, in contrast with previous experimental and computational results for diamond. To better understand the contact stresses that drive the wear, a careful, long-range investigation of contact behavior was also initiated. Since adhesion is crucial in determining contact stresses, an experimental method for the nanoscale measurement of length and strength of adhesive interactions between asperities of arbitrary shape was successfully implemented. |                    |                                |                                   |   |   |
| <b>15. SUBJECT TERMS</b><br>modeling and simulation, multiscale modeling, nanoscale mechanics   |                    |                                |                                   |   |   |
| <b>16. SECURITY CLASSIFICATION OF:</b>  |                    |                                | <b>17. LIMITATION OF ABSTRACT</b> | <b>18. NUMBER OF</b>  | <b>19a. NAME OF RESPONSIBLE PERSON</b><br>CASTER, KENNETH |
| <b>a. REPORT</b>  | <b>b. ABSTRACT</b> | <b>c. THIS PAGE</b>            |                                   |   |   |
| <small>Standard Form 298 (Rev. 8/98)<br/>Prescribed by ANSI Std. Z39.18</small>   |                    |                                |                                   |   |   |

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|              |              |              |     |                    |  |
|--------------|--------------|--------------|-----|--------------------|--|
| Unclassified | Unclassified | Unclassified | SAR | <b>PAGES</b><br>16 | <b>19b. TELEPHONE NUMBER</b> <i>(Include area code)</i><br>+81-42-511-2000 |
|--------------|--------------|--------------|-----|--------------------|--|

**Final Report for AOARD Grant # FA2386-14-1-4071**  
**“Understanding the Atomic-Scale Mechanisms that Control the**  
**Attainment of Ultralow Friction and Wear in Carbon-Based Materials”**

**January 16, 2016**

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**Period of Performance:** 12/16/2014– 12/16/2015

The wear behavior of ultrananocrystalline diamond (UNCD) was characterized at the nanoscale to understand the fundamental mechanisms controlling the initial stages of wear. To enable this, novel nanoscale sliding experiments were conducted *in situ* in a transmission electron microscope (TEM). UNCD is part of a class of materials with tremendous potential for tribological applications due to their low wear and low friction behavior. However, the scientific understanding of the initial wear process is lacking, and this prevents broader application of these materials. The experiments revealed that: (1) the wear follows a gradual, atomic-level removal mechanism, as opposed to fracture or plastic deformation; (2) the rate of wear (rate of material removal) in this nanoscale, single asperity contact is orders of magnitude larger than that measured at the macroscale; and (3) nevertheless, the wear follows the macroscale trend of an initially larger wear rate, followed by stabilization at a lower value. Strikingly, no amorphization during sliding was observed, in contrast with previous experimental and computational results for diamond. To better understand the contact stresses that drive the wear, a careful, long-range investigation of contact behavior was also initiated. Since adhesion is crucial in determining contact stresses, an experimental method for the nanoscale measurement of length and strength of adhesive interactions between asperities of arbitrary shape was successfully implemented.

## **1 Introduction**

Our goal is to characterize and understand the atomic-scale mechanisms governing the tribological behavior (friction and wear) of hard carbon materials during initial sliding

contact, in order to understand what controls and enables the transition from high to low friction and wear. Developing this scientific insight is important to enable widespread usage of these materials to applications such as vibrating joints<sup>1,2</sup>, contacting and sliding surfaces in micro- and nanoelectromechanical systems for sensors and actuators<sup>3</sup>, joints in vacuum or anhydrous environments (as found in the **upper atmosphere and in outer space**), and protective coatings for bearings, bushings, and gears in engines<sup>4,5</sup>, turbines<sup>6,7</sup>, and other aerospace components. The research was carried out using a unique *in situ* transmission electron microscopy (TEM) nanotribometry method that both PI's have collaboratively developed, thanks in part to prior AOARD support. This method allows us to visualize and quantify atomic-level processes occurring in sliding contacts through real time, real space, high resolution TEM measurements of a contact pair, where contact forces are precisely measured and controlled (More details in Section 2.1 and Figure 1).

### 1.1 Current Challenges in Tribology of Carbon-Based Materials

The mechanical and tribological properties of carbon-based films are, under the right conditions, superior to almost all other materials. Diamond, the stiffest and hardest bulk material known, can be grown in a smooth nanocrystalline thin film form with equivalent mechanical performance (ultranano-crystalline diamond - UNCD). These films can exhibit friction coefficients of 0.01 and less (as slippery as ice), and wear rates corresponding to fractions of an atomic layer per pass of the sliding interface ( $<10^{-10}$  mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup>) with no lubricant needed<sup>8-10</sup>. These characteristics far exceed those of well-lubricated interfaces of high performance steels and other expensive coatings.

Despite this potential, the widespread use of these materials is inhibited by a lack of scientific understanding of the initial process of wear, the so-called "run-in" process. While the steady-state wear rate and friction is often low, the *initial* rate of friction and wear during the "run-in" period, can be high. This "run-in" period may consist of only a few cycles of sliding, during which the contacting asperities become smoother, and local stresses, friction, and wear decrease, sometimes by *orders of magnitude*. However, in some cases, this "run-in" continues indefinitely<sup>11-14</sup>. This is a catastrophic outcome: sliding parts can wear out far earlier than expected, or seize. Small changes in load, environment, sliding rate, surface roughness, and sample preparation have been observed to affect whether or not this crucial transition takes place. Results are largely empirical; there is a lack of scientific understanding of the atomic-scale processes in the contact that control whether the transition to low friction and wear occurs. Developing fundamental knowledge of these processes is crucial, and is the key to rationally designing and controlling coatings and operating parameters so that stable, low, reliable friction and wear performance can be obtained for engineered systems using these materials.

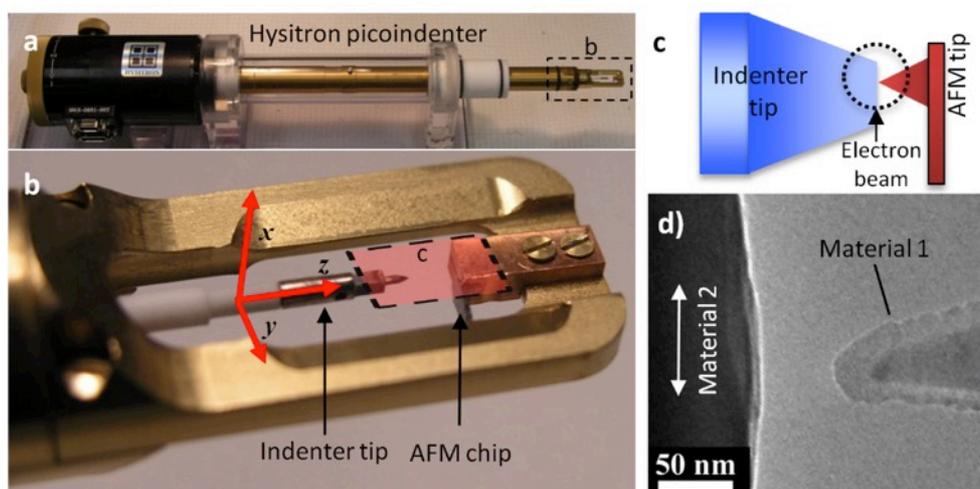
Previous studies by the PIs on interfacial contact conditions including atomic and macro scale studies show that the behavior of individual asperity contacts at the nanoscale plays a critical role in the run-in process<sup>15-19</sup>. More recent research, including by the both PI's, points toward specific atomic-scale mechanisms strongly affecting the sliding behavior of these materials, including: rehybridization from sp<sup>3</sup> to sp<sup>2</sup>-bonding of the C atoms<sup>20</sup>, formation of bonds across the interface and subsequent atomic bond breaking<sup>21</sup>, and the strong passivating influence of small quantities of adsorbates<sup>9,22</sup>. However, many of these observations are indirect or inferred, and others have not been studied in a systematic way that allows understanding of the run-in transition (namely the contact interactions on the surface separation and the real contact area for an asperity) to be investigated.

## 2 Experimental methodology

### Description of the experiment(s)/theory and equipment or analyses.

#### 2.1 *In situ* TEM Tribometry

To address our research goals, over the last few years we have developed a unique *in situ* TEM tribometry method that allows atomic-scale characterization of a single-asperity sliding contact. Both PI's Carpick and Jeng have a Hysitron PI-95 PicoIndenter TEM specimen holder, which was used for this purpose. This instrument measures normal load and displacement simultaneously inside a TEM, and can position an indenter in three dimensions with nanometer scale precision (Figure 1). While the standard configuration is designed for indentation, we developed a method for laterally sliding the indenter (by using integrated piezoelectric controls) against an atomic force microscope (AFM) cantilever. In this configuration, we can study the sliding behavior of several contact pairs (one material in the indenter, other material in the AFM tip) while observing the process with the TEM, allowing atomic-scale resolution of the mechanisms of deformation, adhesion, friction, wear, and failure at the sliding interface.



**Figure 1:** *In situ* TEM setup. (a) The Picoindenter TEM holder. The dashed rectangle is shown in b) in more detail. A piezo tube allows the indenter to attain three dimensional motion with sub-nm resolution. (c) Schematic close up of the AFM cantilever and indenter tip. (d) TEM micrograph of a typical experiment, where characterization of the sliding contact between the material of the AFM tip (#1) and the material of the indenter (#2) can be visualized with high resolution

The *in situ* TEM methodology has the key advantages of live-imaging the process of wear and of resolving volumes removed from the sliding asperity as low as  $25 \text{ nm}^3$  in volume<sup>23</sup>. These capabilities are critical for probing the run-in period of wear. Moreover, since the measurements are carried out *in situ*, the analytical and crystal-characterization capabilities of the TEM can be leveraged to obtain further insights on the wear processes. All these can be done in sequence with sliding experiments to observe and understand the structural changes occurring.

The experimental procedure consists of bringing the indenter surface and AFM tip in contact; the force is controlled by displacing the indenter beyond this point a given amount against the AFM tip, whose spring constant has been calibrated before. Subsequently, lateral sliding motion at a predetermined speed and duration is imposed on the contact. After sliding is finished, the contact is separated. This process is captured on video, allowing

post-processing analysis for metrology of the force and observation of failure events. Furthermore, before and after sliding, high-resolution images of the tip are recorded, thus allowing visualization of volume loss (wear) due to sliding (quantified in post-processing), and of any structural change.

## 2.2 Materials

Our initial plan called for conducting experiments in two materials: Ultrananocrystalline diamond (UNCD) and tetrahedral amorphous carbon (ta-C). However, due to unexpected instrumentation problems, the collaborators producing ta-C were unable to provide samples. Thus, we focused exclusively on UNCD. UNCD is a polycrystalline material with extremely small grains (2-5 nm) with >95% of the carbon atoms bonded in the  $sp^3$  (tetrahedral or diamond) configuration<sup>24,25</sup>. The  $sp^2$ -bonded carbon is found at grain boundaries. We obtained UNCD AFM tips from our industrial collaborators (Advanced Diamond Technologies, Gurnee, IL, USA). During the project, we decided to carry out experiments using single crystal diamond tips (See Section 3.3); these tips were obtained from another industrial collaborator (Adama Innovations, Ireland).

## 3 Results and Discussion

### 3.1 Quantification of UNCD Wear

A significant part of the experimental effort was directed to evaluate the applicability of an atomic-attrition wear model to UNCD. This model has been shown to capture appropriately the wear behavior of silicon (sliding against diamond) using the same experimental methodology, by PI Carpick<sup>23,26</sup>. This model assumes that wear occurs via atom-by-atom removal of surface material through stress-assisted bond formation and breaking. An atom-by-atom wear mechanism assumes a unit process where individual atoms undergo chemical bonding reactions across the interface. The rate of atom loss due to wear,  $\Gamma_{atom-loss}$  [1/s], is then predicted to obey reaction rate theory according to:

$$\Gamma_{atom-loss} = \left\{ \Gamma_0 \exp \left( - \frac{\Delta U_{act}}{k_B T} \right) \right\} \exp \left( \frac{\sigma \Delta V}{k_B T} \right)$$

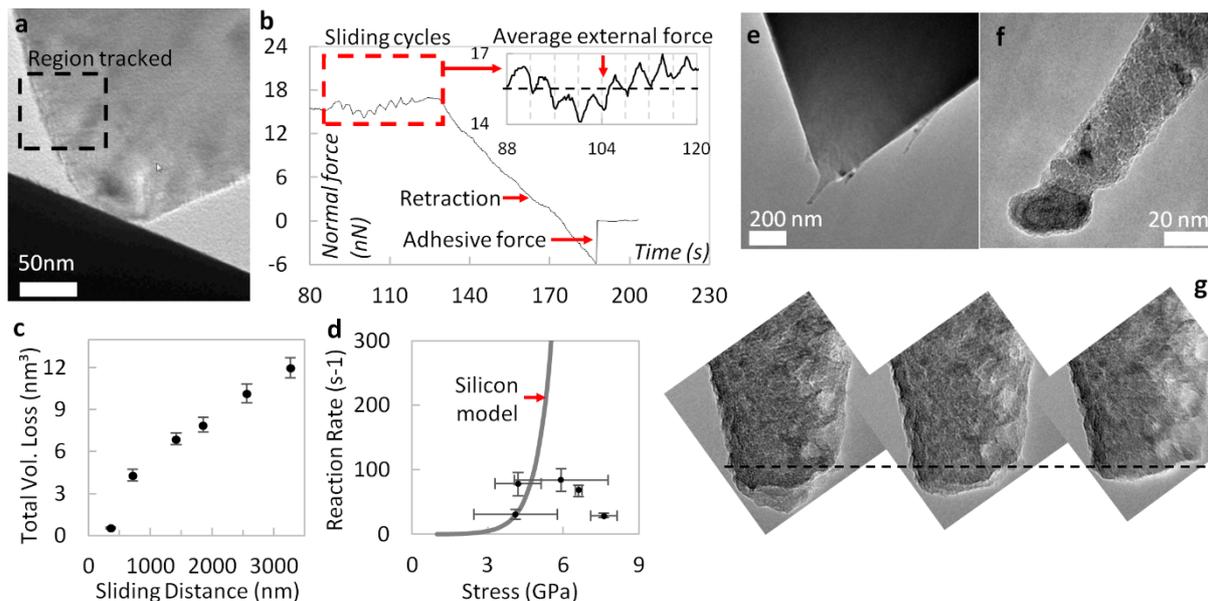
where  $\Gamma_0$  is a pre-factor (an effective attempt frequency),  $k_B$  is Boltzmann's constant, and  $T$  is the absolute temperature. The free energy of activation for the unit process  $\Delta G_{act}$  is reduced by the mechanical work done on the system (due to straining of bonds) according to the relation  $\Delta G_{act} = \Delta U_{act} - \sigma \Delta V_{act}$ , where  $\Delta U_{act}$  is the internal energy of activation (the stress-free activation barrier),  $\sigma$  is the stress component that lowers the energy barrier, and  $\Delta V_{act}$  is termed the activation volume. Given that the model is successful in describing nanoscale wear of silicon<sup>23</sup>, it is promising to evaluate its applicability in UNCD as it may predict the behavior of the material in all conditions, including run-in.

In this project, we improved on our previous methodology by implementing an image tracking algorithm that allows us to measure the displacement of a feature in the UNCD AFM tip throughout the *in situ* TEM sliding experiment (Figure 2a). This improvement allows sub-nN resolution of the contact force; even the fluctuations in normal load arising from sliding cycles are measured (Figure 2b).

By using this improved approach, combined with the volume-loss methodology previously used, which assumes an axisymmetric tip for estimation of the volume loss, we obtained data on the volume loss of UNCD at the nanoscale as a function of sliding distance for a sliding speed of 21 nm/s (Figure 2c). Wear follows a gradual increasing trend, which is encouraging

because it agrees with the prediction of the atomic-attrition wear model.

The data can also be plotted in terms of reaction rate and compared to the previously-validated silicon model (Figure 2d). At low stresses (below 4.5 GPa), the reaction rate for UNCD is, within uncertainty, comparable to silicon. However, for higher stresses, the wear rate is much lower. This indicates that at the nanoscale, UNCD is far more wear-resistant than silicon under harsh conditions. While this is not unexpected, the new advance here is the quantification of the rate. However, the plot also shows that typical UNCD tips (Figure 2a) do not allow to explore the exponential behavior predicted by the model, due to their relatively large tip radius ( $\sim 50$  nm). Furthermore, the large tip radius leads to larger errors in stress estimation than in our previous investigation for silicon.



**Figure 2:** Summary of Results for UNCD wear. See text for description.

To obtain a more refined asperity shape which enables us to achieve higher stresses, our industrial partners (ADT and Adama) collaborated to provide UNCD tips with a much smaller tip radius using an advanced, novel processing method. These *sharpened UNCD probes* (Figure 2e) are produced by subjecting conventional UNCD AFM probes to gallium ion irradiation in a small area of the probe's apex; this amorphized area serves as a mask for subsequent plasma etching of the probe. The end result is a UNCD tip with a sharp pillar-like protrusion (diameter of  $\sim 25$  nm; Figure 2f) and a small tip radius, ideal for high-stress wear testing. *In situ* TEM testing of these probes has been conducted; an example is shown in Figure 2g.

The testing of these probes is ongoing, which continues under our newly awarded AOARD project. The preliminary results shown in Figure 2g suggest that although wear is progressive and well resolved, some electron-beam damage is occurring in these sharp UNCD tips while the experiment is conducted. This damage may be occurring as a result of the sharpening process. We are working with Adama to understand these effects. Although this damage is undesirable, the sharpness of these tips is a necessary characteristic to probe the high-stress wear regime.

We also made progress in studying boron-doped UNCD. Boron-doping endows UNCD with electrical conductivity, which broadens its applications including for contact electrode applications, for example. Working with ADT, we developed and characterized a new

version of boron-doped UNCD that could be grown at lower temperatures<sup>27</sup>. In collaboration with CCU, we have characterized the mechanical properties (modulus, hardness) of this new material (work still in process) and now plan to measure its wear behavior in comparison to conventional UNCD.

### 3.2 Evolution of UNCD single-asperity wear rate

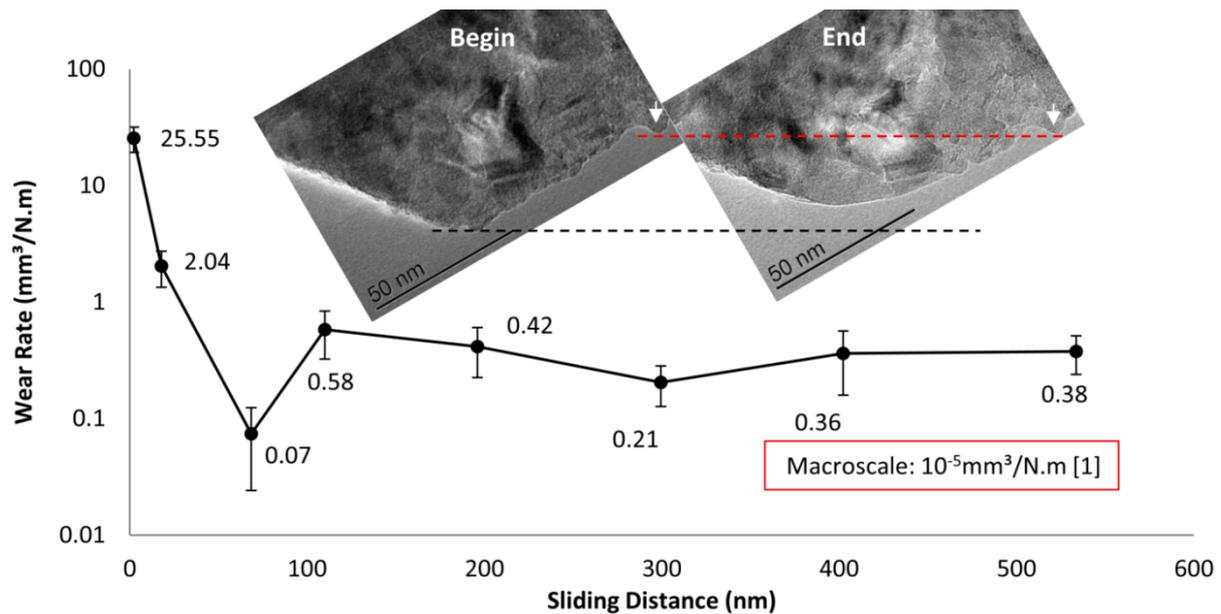
Besides the quantification of wear using the nanoscale model explained in the previous section, it is also possible to quantify a conventional “Archard” wear rate, defined as:

$$K = \frac{V_{Loss}}{Fd}$$

where  $V_{loss}$  is the volume lost by sliding the asperity over a distance  $d$ , applying a force  $F$ . This wear rate is typically used in macroscale experiments<sup>28</sup>; therefore a comparison of its values in nanoscale versus macroscale experiments is a useful first step to understand how the single-asperity contact (nanoscale) controls the run-in behavior at the macroscale.

The results are shown in Figure 3. The wear rate is high at the beginning of the experiment, and rapidly reduces to a steady state value. Interestingly, this nanoscale behavior mimics the behavior of friction and wear during the macroscale run-in process<sup>9,29</sup>. However, the values of the wear rate are orders of magnitude higher than what is reported at the macroscale ( $0.07\text{-}25.55$  vs.  $10^{-5}$  mm<sup>3</sup>/N.m)<sup>21</sup>. A full comparison of wear rates across length scales requires application of multiscale contact mechanics models, which have only recently been developed for cases where adhesion is present<sup>30</sup>; this comparison will be conducted in the new project. Differences between the conditions in the nanoscale and macroscale experiments must also be considered, namely the different atmospheres (high vacuum vs. dry/humid air) and sliding speeds ( $\sim\text{nm/s}$  vs.  $\sim\text{mm/s}$ )<sup>21</sup>. Regardless, this observation indicates that the nanoscale single asperity experiments may indeed capture the harsher contact conditions seen at the outset of macroscale sliding.

Further experiments are ongoing to understand whether the single-asperity wear rates are consistently higher for different tips, and whether surface treatments to the tip have an effect on wear rate. In particular, hydrogen plasma treatment of the tips will introduce hydrogen at the surface, which is known to promote faster run-in and lower steady state friction and wear rates at the macroscale<sup>21</sup>, and is therefore a way to mimic the lubricating humid atmosphere present in macroscale experiments, in the vacuum of the TEM.

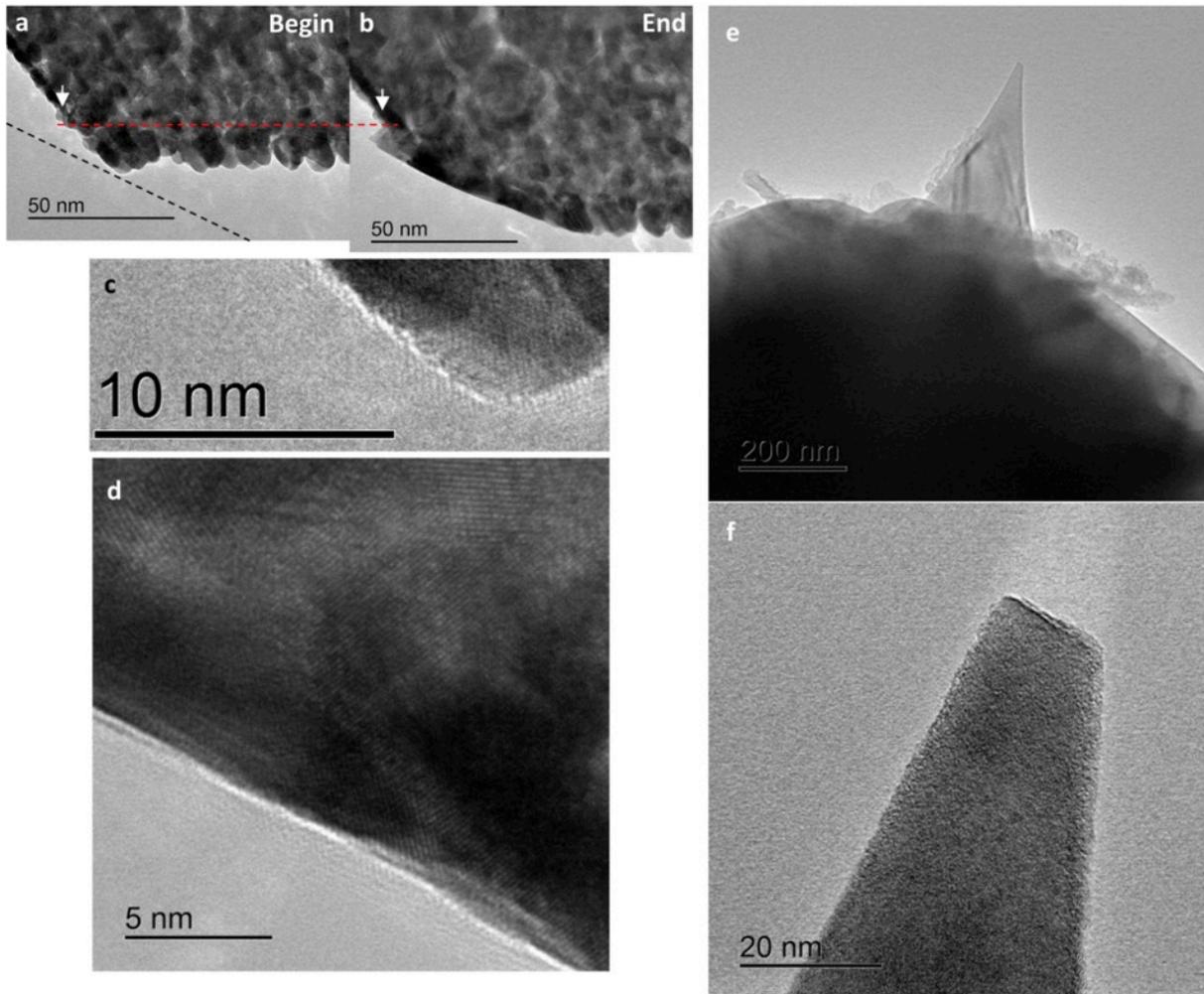


**Figure 3:** Behavior of the wear rate for single asperity UNCD. The values are significantly larger than macroscale wear rates. Inset TEM pictures show the state of the asperity at the beginning and at the end of the experiment. The white arrow and red line indicate an unchanged feature for reference. The black line helps to indicate the amount of wear observed.

### 3.3 Morphological behavior during wear

*In situ* TEM also allows observation of the morphology of the asperity as sliding progresses. An example is shown in Figure 4. One striking aspect is that despite the dramatic geometrical changes of the asperity, the crystalline character of the UNCD is preserved throughout the tip as evidenced by the lattice fringes (Figure 4c-d). These observations are in sharp contrast with previous macroscale experiments and nanoscale simulations of diamond sliding contacts, which indicate the development of an amorphous layer at the sliding interface, thought to be responsible for the low-friction, low wear behavior<sup>31,32</sup>. This is consistent with our previous observations on silicon<sup>33</sup>.

We have aimed to simplify the interpretation of this surprising behavior by performing sliding experiments using single-crystal diamond tips. The experiment is simplified because only one grain is in contact and there is no pre-existing amorphous carbon in the tip. Thus, visualization of the lattice is easier to interpret. A picture of a single crystal tip is shown in Figure 4e-f. Initial results are promising, and experiments on these samples are ongoing in the context of our current AOARD support.



**Figure 4:** Evolution of UNCD morphology. a-b) Beginning and end of a sliding test. The white arrow and red line indicate an unchanged feature for reference. The black line helps to indicate the position of the surface against which the tip was slid. c-d) Zoomed-in images of the edge of the tips in a and b, respectively. e-f) Single crystal diamond tips for further experimentation.

### 3.4 Length and Strength of Adhesive Interactions between Silicon and Diamond

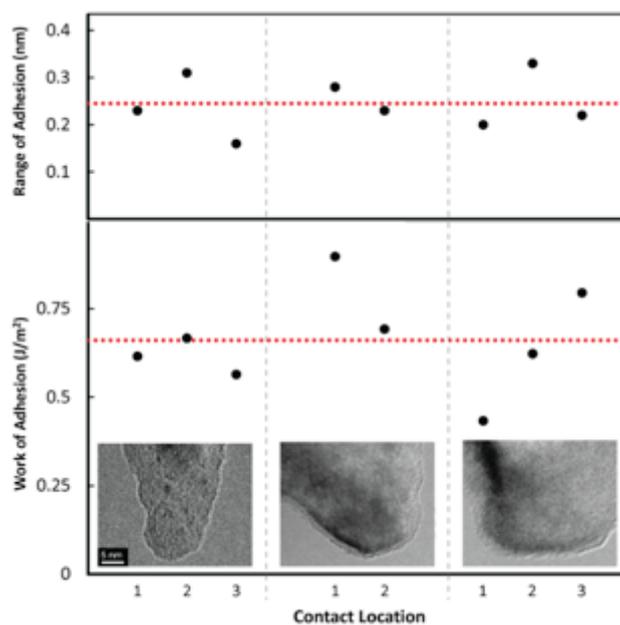
Adhesion between solids at the nanoscale has a tremendous effect on contact stress and consequently on wear. In the above discussion and prior publications<sup>33</sup>, only the mean contact stress was used to analyze the reaction rate. However, a full description of the inhomogeneous stress *distribution* is needed. This requires, among other things, a description of the adhesive interactions between the solids in contact. At a minimum, two parameters are needed to describe the adhesion behavior of solids, the “length” and “strength” (adhesive range and work of adhesion, respectively). The latter is readily measurable while the former has rarely been determined from experiments. In many studies, the length scale is estimated using order-of-magnitude arguments, then the work of adhesion is calculated based on this estimated value. However, the quality of calculated results and even the applicability of the chosen model are very sensitive to errors in this estimated parameter.

With partial support from AOARD, we developed a novel experimental technique to simultaneously determine both the work of adhesion and range of adhesion<sup>34,35</sup>. The experiments were conducted for the silicon-diamond contact pair, but the method is general and will be applied to the UNCD-diamond system we are working with presently. This

capability is important to understand the role of adhesion itself, and the resulting contact stresses on wear in diamond-diamond contacts.

Adhesion measurements were conducted using the experimental setup described in Section 2.1. Nanoscale silicon asperities were brought into contact and separated from a flat diamond substrate. The pull-off force and snap-in distance were measured with sub-nanonewton and sub-nanometer resolution, respectively. TEM imaging allowed characterization of the detailed shape of the asperity with sub-nanometer resolution immediately before and after contact (Fig. 3); this is a novel aspect of the work since previous efforts assumed the tip had a smooth, spherical shape. In most cases, the true shape deviates significantly from this assumption.

A simple analytical model is then used to integrate an adhesion interaction potential over the real shape of the asperity. Next, by fitting the model results to experimentally measured pull-off forces and snap-in distances for a variety of asperity shapes, the values of work of adhesion and range of adhesion are determined. These fundamental parameters describe the adhesive interaction between silicon and diamond, and allow the prediction of adhesive forces between arbitrary geometries. These results not only serve to demonstrate the applicability of continuum-based models to nanoscale asperities, but they also demonstrate a general method by which the adhesive interaction between two materials can be experimentally characterized.



**Figure 5:** Values of work of adhesion and range of adhesion are extracted simultaneously from *in situ* adhesion tests. The extracted values of work of adhesion (a) and range of adhesion (b) are shown from three different tips (TEM images shown at bottom).

The results are shown in Figure 5. The measured value of intrinsic work of adhesion,  $0.66 \pm 14 \text{ Jm}^{-2}$ , was significantly higher than most previous experimental and simulation measurements. However, we explicitly account for surface roughness down to the sub-nanometer scale, unlike previous measurements. Importantly, this value is 70% higher than the value that would have been measured under assumptions that are common in AFM testing (parabolic tip, DMT model). This demonstrates the critical importance of accounting for Ångstrom-scale roughness in nanocontacts. The measured range of adhesion,  $0.25 \pm 0.06 \text{ nm}$ , represents the most direct experimental measurement of this quantity to date. It falls

within the range of previous measurements, but is larger than the value predicted using the common estimation that the range of adhesion is equal to the atomic spacing of the component materials.

### 3.5 Knowledge Transfer between the Collaborating Groups (Penn-CCU)

To strengthen collaboration between the two PI's and ensure exchange of best practices for carrying out experiments, PI Carpick and his postdoc Dr. R. Bernal visited CCU from July 15-17, 2015. During this visit, Penn personnel trained new personnel at CCU assigned to this project (Masters Student Polun Chen and Postdoc Qingkang Liu) on operation of the Picoindenter and TEM. The PIs and project participants also discussed and developed plans for experiments and joint publications. Finally, Penn personnel provided UNCD samples for CCU to test. Pictures from the visit are shown in Figure 6.



**Figure 6:** Interactions between the PI's and project participants during Penn's personnel visit to Taiwan.

## 4 List of Publications and Significant Collaborations that resulted from AOARD support

### 4.1 Papers Published in Peer-Reviewed Journals

1. Jacobs, T.D.B., Lefever, J.A. and Carpick, R.W. Measurement of the Length and Strength of Adhesive Interactions in a Nanoscale Silicon–Diamond Interface. *Advanced Materials Interfaces* **2** (2015).
2. Jacobs, T.D., Lefever, J.A. and Carpick, R.W. A Technique for the Experimental Determination of the Length and Strength of Adhesive Interactions between Effectively Rigid Materials. *Tribol. Lett.* **59**, 1-11 (2015).
3. Zeng, H., Konicek, A.R., Moldovan, N., Mangolini, F., Jacobs, T., Wylie, I., Arumugam, P.U., Siddiqui, S., Carpick, R.W. and Carlisle, J.A. Boron-Doped Ultrananocrystalline Diamond Synthesized with an H-Rich/Ar-Lean Gas System. *Carbon* **84**, 103-117 (2015).

### 4.2 Papers Published in Non-Peer-Reviewed Journals or in Conference Proceedings

None

### 4.3 Conference Presentations

1. **Invited.** *New Views of Adhesion and Wear from In-Situ TEM Studies of Nanocontacts.* R.W. Carpick, Symposium for MEXT Project on Nano Mechanical Characterization Method by MEMS Devices and In-situ TEM Observation, University of Tokyo, Tokyo, Japan, Jan. 2014.

2. **Invited.** *Friction and wear: New insights from atomic-scale measurements.* R.W. Carpick, National Institute for Materials Science (NIMS), Tsukuba, Japan, Dec. 2015.
3. **Invited.** *Atomic-Scale Processes in Single Asperity Friction and Wear.* R.W. Carpick, Midwest Mechanics 2014/2015 Invited Speaker, Iowa State University, Feb. 2015.
4. **Invited.** *Atomic-Scale Processes in Single Asperity Friction and Wear.* R.W. Carpick, Midwest Mechanics 2014/2015 Invited Speaker, University of Minnesota, Feb. 2015.
5. **Invited.** *Atomic-Scale Processes in Single Asperity Friction and Wear.* R.W. Carpick, Midwest Mechanics 2014/2015 Invited Speaker, Purdue University, Mar. 2015.
6. **Invited.** *Atomic-Scale Processes in Single Asperity Friction and Wear.* R.W. Carpick, Midwest Mechanics 2014/2015 Invited Speaker University of Illinois Urbana-Champaign, Mar. 2015.
7. **Invited.** *Atomic-Scale Processes in Single Asperity Friction and Wear.* R.W. Carpick, Midwest Mechanics 2014/2015 Invited Speaker, Illinois Institute of Technology, Mar. 2015.
8. **Invited.** *Friction and Wear: New Insights from Atomic-Scale Measurements.* R.W. Carpick, University of Maryland, Baltimore County, Mechanical Engineering Dept., Apr. 2015.
9. **Invited.** *Friction and Wear: New Insights from Atomic-Scale Measurements.* R.W. Carpick, Tufts University, Mechanical Engineering Dept., Apr. 2015.
10. **Invited.** *Contact at the Nanometer Scale: New Insights into Adhesion, Friction, and Wear.* R.W. Carpick, Gordon Research Conference on Nano-Mechanical Interfaces, Hong Kong, Jul. 2015.
11. **Contributed.** *Atomic-level studies to elucidate fundamental tribological properties of ultrastrong carbon-based materials* R. A. Bernal, K. E. Ryan, P.L. Keating, T.D.B. Jacobs, Z. Milne, J.A. Harrison, R.W. Carpick, Gordon Research Conference on Nanomechanical Interfaces. Hong Kong, July 2015.
12. **Invited Keynote.** *Atomic-scale Tribology Elucidated by In Situ Approaches.* R.W. Carpick, T.D.B. Jacobs, N.N Gosvami, J.A. Bares, F. Mangolini, A.R. Konicek, D.G. Yablon, International Tribology Conference, Tokyo, Japan, Sept. 2015.
13. **Invited.** *Achieving Ultralow Friction in Carbon-Based Materials: The Roles of Environment, Surface Chemistry, System Stiffness, and Speed.* XIN Workshop on Superlubricity, Beijing, China, Oct. 2015.
14. **Contributed.** *Fundamental Insights on Friction and Wear of Ultrastrong Carbon-based Materials* R. A. Bernal, T.D.B. Jacobs, Z. Milne, K. Wu, Y. R. Jeng, G. Cross, R.W. Carpick, , American Society of Mechanical Engineers – International Mechanical Engineering Conference and Exposition (ASME-IMECE), Houston, TX, Nov. 2015.
15. **Invited.** *New Insights into Friction and Wear through In-Situ Nanotribology.* Joint Symposium of the Surface Science Society of Japan and the Vacuum Society of Japan (SSVS), Tsukuba, Japan, Nov.-Dec. 2015.

#### 4.4 Manuscripts Submitted but not yet Published

None

#### 4.5 List of Interactions with Industry or with Air Force Research Laboratory (AFRL) scientists or significant collaborations that resulted from this work

- Industrial collaborations with Advanced Diamond Technologies Inc. (Gurnee, IL, USA), and Adama Innovations LLC (Ireland), on the development of diamond nanostructures for AFM probes.
- Collaborating with Hysitron Inc. (Minneapolis, MN, USA) on developing *in situ* tools.
- AFRL collaboration with Chris Muratore & John Bultman, AFRL, on tribology of 2-D materials, in connection with ongoing AOARD award (FA2386-15-1-4109).

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