Molecular Dynamics Examination of Sliding History-Dependent Adhesion in Si–Si Nanocontacts: Connecting Friction, Wear, Bond Formation, and Interfacial Adhesion

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Abstract
We simulate the contact between nanoscale hydrogen-terminated, single-crystal silicon asperities and surfaces using reactive molecular dynamics (MD) simulations. The results are consistent with recent experimental observations of a more than order-of-magnitude sliding-induced increase in interfacial adhesion for silicon-silicon nanocontact experiments obtained using in situ transmission electron microscopy (TEM). In particular, the MD simulations support the hypothesis that the increased adhesion results from sliding-induced removal of passivating species, in this case hydrogen, followed by rapid formation of Si–Si covalent bonds across the interface, with little plastic deformation of the asperities. The MD results concur with the additional hypothesis that subsequent readesorption of passivating species explains the experimental observation that adhesion reverts to low values upon subsequent contact. However, the simulations further reveal that the sliding-induced adhesion increase is only observed when there are a sufficient number of preexisting surface defects in the form of incomplete hydrogen coverage. Increased hydrogen coverage suppresses interfacial bonding, within the time span of the simulations. Furthermore, the relative alignment of the surface crystal axes plays a strong role in affecting the probability of bond formation during sliding and the subsequent adhesive pull-off force. Also, the hydrogen coverage and sliding distance significantly impact friction at low to moderate hydrogen coverages. Atomic-scale wear does occur during the sliding process primarily through Si–Si bond formation across the interface followed by pull-out of Si atoms from the tip. At low hydrogen coverages, wear is far more severe, Archard’s wear law is obeyed, and significant morphological changes of the asperity occur. The bond formation process is highly stochastic, but shows a general trend of greater numbers of bonds with greater sliding distances. Tips wear by losing large clusters of material, then smaller clusters and individual atoms, and eventually enter into a wearless regime as hydrogen termination increases.

Graphical Abstract
A hydrogen-terminated Si tip (green and blue) in sliding contact with a hydrogen-terminated Si substrate (yellow and red). The sliding direction is indicated by the black arrow. At this level of hydrogen termination, wear is initiated by the removal
of hydrogen atoms from the tip (blue atoms at left of figure). Continued sliding causes the formation of interfacial Si-Si bonds followed by the transfer of Si and H from the tip to the surface.

Keywords Adhesion · MD simulations · ReaxFF · Friction · Atomic-scale wear mechanisms · Pull-off force · Silicon-silicon nanocontact

1 Introduction

Buried solid interfaces, which are difficult or impossible to directly observe, often undergo complex processes which manifest as wear, friction, and adhesion. Uncovering the mechanisms underlying these tribological processes is critical for understanding phenomena occurring on a large range of length scales, from modeling and predicting earthquakes [1–4] to making more durable tools for extreme environments [5–7]. At the nanoscale, such knowledge can benefit emerging scanning probe-based manufacturing techniques—such as pick-and-place printing [8] and tip-based nanolithography [9–11], which have the potential to supplement or disrupt traditional nanolithography techniques.

Prof. Mark O. Robbins was a pioneer and a master in elucidating the fundamental processes in tribology, both through atomistic and multiscale simulations of these processes at the buried interface, and through his deep, physically based insights which were broadly applicable to systems in very generalizable yet accessible ways. He considered multiple forms of matter in tribology: hard contacts in dry conditions (e.g., Refs. [12, 13]), and with contaminants (e.g., Refs. [14]); liquid lubricants under compression and shear (e.g., Refs. [15–17]); and soft materials in contact, including the change in behavior as one goes from soft or compliant to hard and stiff (e.g., Refs. [18, 19]). Prof. Robbins was particularly eager to support and promote collaborations and comparisons between experiments and simulations, as he valued the validation experiments could bring to simulations, and understood the unique insights simulations could bring to experiments where the buried interface was hidden from view. He also supported and promoted experimental work that pushed the boundaries of established methods, and took an interest in in situ studies. All of the authors of this paper benefited from Prof. Robbins’ feedback, questions, challenges, and insights on our prior simulation and in situ experimental tribology work. Inspired by his accomplishments and interest in linking simulations with in situ experiments, here we have collaborated to provide a study that uses these approaches to gain new insights into mechanisms of contact, adhesion, friction, and wear for silicon-silicon nanocontacts.
Silicon is an element found in all of the previously mentioned probe-based manufacturing examples and, though silicon and its compounds are one of the most widely utilized and studied materials, understanding of the chemistry at solid silicon and silicon compound interfaces subjected to applied forces is still lacking. This deficit in tribochemical knowledge is underlined, for example, by the recent observation of an unexpected phenomenon, whereby the magnitude of adhesion between oxide-free silicon asperities, measured in a high vacuum transmission electron microscope (TEM), was reproducibly observed to depend on whether sliding had occurred prior to separation; the so-called “reversible” or sliding history-dependent adhesion [20]. In those experiments, the oxide on the tip was fractured off or removed by sliding in the TEM immediately before experiments, and did not regrow. Adhesion was small when measured with the traditional indentation test i.e., with no sliding, but on average more than on order of magnitude larger when measured after some sliding had occurred. It was hypothesized that sliding removes a passivating layer, exposing bare and reactive silicon atoms on opposite surfaces to one another, allowing them to form covalent bonds. These covalent bonds require a larger force to separate than can be attributed to purely van der Waals attractions, the latter being the source of adhesion in tests without sliding and the former with sliding. Thus, the adhesion or “pull-off” force would be greater for sliding, often by varying amounts depending on the trial, indicating a stochastic nature to the bond formation events, similar to what was observed in MD simulations of DLC-diamond nanocontacts [21]. Even with the capability to observe the edges of the silicon contacts in TEM, the contact interface was always buried, precluding observation of the cause of the reversible adhesion phenomenon. In this work, we present results from molecular dynamics (MD) simulations that explore the buried silicon interface in the presence of varying hydrogen termination concentrations. The simulations show that hydrogen plays a key role in the adhesive behavior of silicon, with and without sliding.

### 2 Computational Details

Classical MD simulations were conducted to better understand the atomistic processes that control adhesion and friction. The simulations were designed to match the experimental conditions as outlined in the Si–Si nanocontact study by Milne et al. [20] as closely as possible. While it is possible to match variables, such as, material types, applied loads, and tip size, the overlap of some variables, such as sliding speed, is still not feasible. While experimental contact sizes are typically larger than those used in MD simulations, creative approaches such as modified tip geometries can be used to match contact sizes [22]. Using this approach, the simulations provided insight into the observed experimental trends and the mechanisms at play. This approach has been successful in a number of previous comparisons between experimental nanocontact experiments and MD simulations of adhesion [21–25].

#### 2.1 Simulation Setup and Configuration

A representative simulation setup is illustrated in Fig. 1. A hydrogen-terminated silicon (111) surface, 15nm by 15nm in the contact plane, and 2.5 nm thick, was used as the contacting surface. The silicon used in the simulations was terminated with hydrogen based on results from previously published measurements using the same experimental setup which indicate that the silicon indenter, like typical silicon crystals, is largely passivated with hydrogen with a 1 × 1 adsorbate structure due to ambient exposure to ambient conditions [26, 27]. In experiments, this termination may not be complete and may include defects, which are known to affect adhesion of silicon and diamond surfaces (Note, that diamond has a similar 1 × 1 H-termination as silicon.) [21, 28–30]. The presence of defects in the experiments was modeled by changing the percentage of hydrogen termination in the simulations. Other contaminants, especially water and hydrocarbons, are likely present in the experiments. Fully modeling the effect of these other species with reliable reactive potentials is beyond the scope of the present work. Also, oxide growth is unlikely under the experimental conditions described by Milne et al., and the oxide layer initially present on the Si surfaces was removed prior to conducting their TEM experiments [20]. Moreover, as we show below, the generic mechanism of increased adhesion is sliding-induced removal of passivating species, which could operate in a similar manner regardless of adsorbate species. Thus, our goal here is to use H as a prototypical passivating species to examine whether the resulting mechanism is consistent with the observed experimental observations.

The method used to generate tips for the MD simulation has been described in several previous publications [21, 23, 31–33]. The tip is modeled as an axisymmetric punch with a power-law profile. The power-law profile is described in cylindrical coordinates as:

$$z = \frac{r^N}{R N^1_Q}$$  \hspace{1cm} (1)

where $z$ is the vertical coordinate or height, $r$ is the radial coordinate, and $N$ is the power-law index. Following the convention of Grierson et al. [33], the substitution $Q = S^{N-1} R N^{-1}$ is used here, where $S$ is a dimensionless parameter that describes the steepness of the power-law tip profile and $R$ is an effective tip radius with dimension of length regardless of $N$. The tips used in this study used initial
values of $N = 5$, $S = 1$, and $R = 2.5$ nm to carve a tip from a block of silicon oriented such that the tip axis is along the [111] crystallographic direction. The tip height is 3.0 nm. The experimental AFM tips in Milne et al. are also (111) terminated, but best fits of the power-law profile had a value of $N = 2$ [20]. Slightly flatter tips (i.e., with a higher power-law exponent) were used in the MD simulations because the simulated tip is smaller than the experimental tips due to computational constraints mentioned above, which would result in significantly fewer atoms coming into contact with the substrate in the simulations than in the experiments. To compensate for this difference, the value of $N$ used in the simulations was increased, allowing more atoms to come into contact. The as-cut tip has a flat, atomically smooth (111) crystal facet at its apex. After cutting, the tip was annealed to promote surface reconstruction particularly on the sides of the tip. One other change from the experimental configuration is the use of one tip and one flat surface, instead of two tips in contact. This simplifies the geometry of the problem, permitting sliding to be constrained to one linear direction, and thus facilitated easier interpretations of the mechanisms at play. Furthermore, most of the experiments involved lateral sliding distances that were small compared to the tip radius. As well, the experiments included cases where one tip was much larger in radius than the other. The experimental behavior was consistent among all of these cases. Thus, we do not expect this modification of the geometry to have any substantial effect on the results.

Surface sites on both the tip and the substrate were randomly selected for hydrogen termination so that both had equal percentage coverages. Matching hydrogen coverages of 20, 40, 50, 60, 80, 90, and 100% were examined here; the example shown in Fig. 1 is for 20% coverage. Adhesion is known to exhibit a dependence on crystallographic orientation and alignment, particularly at the atomic scale. Atomic-scale friction may also show a dependence on sliding direction [34–40]. To account for these orientation effects, two tip orientations were investigated. In the first case, the crystallographic orientation of the tip and substrate are aligned such that the [110] direction of tip and substrate both aligned parallel to the $x$-axis. In the non-rotated tip case, the two surfaces are in registry and fit together almost perfectly as a matched pair, analogous to a lock and key. In the second case, the crystallographic axes are misaligned by rotating the tip by 90° about the tip’s vertical axis such that the [110] axis of the substrate remains in the $x$-direction and the [110] axis of the tip is now in the $y$-direction. In this case, the two opposing surfaces are out of registry. The non-rotated and rotated tips were selected to represent two possible extremes in both adhesion and friction with the non-rotated tips expected to be higher due to in-registry lattice locking [29]. Throughout the remainder of this paper, the aligned tip is referred to as “90° rotated”. Before starting the simulations, the lowest atom on the tip was placed 0.50 nm above the highest atom on the substrate.

The ReaxFF potential was used to model interatomic forces with a recently updated parameter set for Si/C/H containing systems that was optimized for Si surfaces [41]. The ReaxFF is a reactive empirical bond-order-dependent potential that includes non-bonded van der Waals and Coulomb interactions with variable charge. The bond order and non-bonded interactions make the ReaxFF potential valuable for studying friction and adhesion of materials. The ReaxFF potential has been ported to the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [42]. The LAMMPS MD code has domain-decomposition schemes that allow parallel simulations to run efficiently on thousands of processors. The equations of motion were integrated using the velocity Verlet algorithm [43] in LAMMPS.

### 2.2 Simulation of Adhesion and Friction

Simulations were carried out by first minimizing the energy of the tip-substrate system using a conjugate gradient minimization scheme in LAMMPS [43, 44] to allow for tip and surface reconstruction after tip cutting and H-termination. Next, a series of Indent-Hold-Retract (IHR) simulations were carried out on all of these tip-substrate systems in the following way. The system was first thermalized at 300 K for 25 ps to ensure a uniform distribution of temperature throughout the system. Temperature was maintained at 300 K by applying a Berendsen thermostat [45] to the atoms in the red layers shown in Fig. 1. A constant velocity of 0.020 nm/ps was then applied to the rigid layer of the tip (blue atoms) to move the tip closer to the substrate until a preset
target load of 10.0 nN was achieved. The tip was then held at the target load for 10,000 steps, or 2.5 ps, and then retracted from the substrate by moving the rigid layers of the tip at a constant velocity of 0.020 nm/ps away from the substrate. The IHR simulations described above allow for adhesion and covalent bonding between the tip and the substrate to be studied in the absence of sliding. Because it is difficult to bring the tip and the substrate together in a perfectly perpendicular arrangement during an AFM experiment, some sliding, or lateral motion of the tip, does occur whenever the tip and substrate may contact. To study the effect of sliding on adhesion, tips were also slid for 10.0 nm under a constant load of 10.0 nN at 0.020 nm/ps. The velocity is applied such that the tip travels 3 units in the x-direction for every 1 unit in the y-direction as indicated by the vector $\mathbf{V}$ shown in Fig. 1. This ensures that the periodic image of the tip does not pass over previously worn areas of the substrate and, therefore, allows for a larger distance sliding with a smaller system size. The effect of sliding direction on the substrate on friction was not considered in this work but will be the subject of a subsequent publication.

In the prior experiments, in situ measurement of adhesion during sliding is not possible. Rather, to measure adhesion, sliding is interrupted, the tip is separated from the surface, and then the tip placed back in contact before resuming sliding. Due to instrument drift, repositioning the tip exactly where it left off is difficult or impossible. In addition, removing the tip from the substrate to measure adhesion may result in transfer of atoms from the tip to the surface, or vice versa, which means that the tip is not exactly the same before and after breaking contact. MD simulation has an advantage over experiment in that the coordinates of all atoms are known at all times. These coordinates can then be captured at specified times and used as starting configurations for new sets of simulations with no interruption of the sliding process. In the simulations described here, the atomic coordinates were captured after 2.5, 5.0, 7.5 and 10.0 nm of sliding. These snapshots were then used to determine the adhesion at these points. The simulation procedure for each subset was as follows. First, the center of mass velocity of the tip was set to zero to remove the sliding velocity. The tip was then held in place at a constant load of 10.0 nN for 2.5 ps and then retracted from the substrate by moving the rigid layers upwards at a constant velocity of 0.020 nm/ps. As mentioned above, instrument drift makes it difficult or impossible to place the tip back in exactly the same spot after the tip is removed for an adhesion measurement. To determine the degree to which this affects adhesion, the tips were removed from the surface after 10 nm of sliding and then replaced over a new location on the substrate that had not been disturbed by sliding, then the IHR sequence was repeated. The simulation sequence is illustrated schematically in Fig. 2a. Friction force, normal forces, and atomic trajectories are collected during sliding and each adhesion measurement for further analysis. The load and the friction forces are taken as the sum over all tip atoms perpendicular to the surface and in the sliding direction, respectively. Force data are collected every 5 MD time steps. After MD 100 time steps (0.025 ps), the forces are averaged and output. Atomic trajectories (i.e., positions and velocities) are captured every 0.25 ps. An example plot of friction versus the distance slid is given in Fig. 2b. To produce the smoothed curves shown in Fig. 2a
and c, a 21 point running average filter was applied to the force data.

Adhesion is measured in terms of the pull-off force and taken to be the minimum in the force versus displacement curve upon retraction of the tip from the substrate, which is same definition that has been used in previous publications [21, 31, 46]. An example set of normal force versus the vertical tip displacement curves for each point along the slide are illustrated in Fig. 2c. In the absence of covalent bonding, the pullback portion of the force curve is smooth and there is typically a single, well-defined, minimum, which has also been observed in other tip-substrate simulations [31]. In the presence of covalent bonding between the tip and the substrate, the force curve can have multiple extrema arising from the formation and subsequent breaking of covalent bonds [46], complicating the definition of pull-off force. The conditions leading to the formation of these interfacial bonds are discussed below. In all cases, the reported pull-off force is taken to be the largest minimum in the pullback force curve. Likewise, in the experiments, the maximum observed tensile force before separation is used as the reported adhesion force. Because energy is dissipated as the covalent bonds are broken during pullback, we further quantify differences in the force versus distance curves by integrating the area below zero force to produce the work expended to separate the tip and surface, and dividing by the area of contact measured at a nominal load. Strictly speaking, this does not correspond to the work of adhesion given the shape of the contacting bodies; however, as the tip is rather flat, the value obtained is approximately equal to the work of adhesion. More broadly, it provides an approximate way to compare the energy per unit area dissipated when separating the tip from the surface.

3 Results and Discussion

3.1 Adhesion in the Absence of Sliding

The IHR simulations allow for the examination of the effects of hydrogen termination and tip registry on adhesion in the absence of sliding. Fig. 3a shows the pull-off forces for non-rotated and 90° rotated tips as a function of hydrogen termination. Several notable observations are apparent from the data shown in Fig. 3a. First, reducing the hydrogen coverage generally increases pull-off forces. This behavior has been observed in previous MD simulations for diamond-diamond, diamond like carbon (DLC)-diamond, and ultrananocrystalline diamond (UNCD)-diamond surfaces in contact [29, 47] as well as an AFM-MD study examining adhesion between a DLC tip and a diamond(111) substrate [21, 23], and silicon (111) tip and diamond (111) substrates [46]. MD simulations have also examined the effects of roughness, hydrogen termination and material type on adhesion between hydrogen-terminated DLC and UNCD tips interacting with diamond(111), DLC, and UNCD surfaces, with and without H [31]. Note that the present study differs from the previous examinations not only in the identity of the tip-substrate couple, but because the degree of hydrogen termination on the tip and surface is matched.

This increase in pull-off force as a function of hydrogen termination is attributed to the increase in unsaturated Si sites available for covalent bonding as H-termination is decreased, and to the associated small changes in roughness that allow tip and substrate atoms to approach more closely, giving rise to an increased opportunity for bonding. The number of Si–Si bonds between the tip and substrate as a function of hydrogen coverage is shown in Fig. 3b. In this analysis, Si–Si pairs are assumed to be bonded when they are within 0.2775 nm of each other, and silicon-hydrogen pairs are assumed to be bonded when a Si-H pair is within 0.1975 nm of each other. These values are chosen to be half-way between the minimum and maximum covalent cut-off values of bond lengths in the second generation REBO potential for Si, C, and H, i.e., the point where the bond cut-off interaction term \( F_{ij} \) is equal to 0.5 for the respective bonds [48]. For diamond cubic Si, 0.2775 distance corresponds
to approximately one quarter of the way between first and second nearest neighbors and represents a reasonable limit for the range of covalent bonding. For reference, the Si–Si equilibrium bond length in diamond cubic Si is 0.2351 nm [49] and Si-H equilibrium bond length in SiH4 is 0.148 nm [50]. As expected, the number of bonds present during contact increases with decreasing H-termination. As has been shown previously, covalent bond formation between the tip and the substrate has a stochastic component and the variability of the bond formation increases as the hydrogen content decreases [21]. This gives rise to the small amount of scatter in the plots.

Second, the pull-off forces tend to be higher for the non-rotated tips. This is consistent with prior studies on other H-terminated materials. Specifically, Piotrowski et al. [29] examined the work of adhesion when infinitely flat, self-mated diamond surfaces were brought into contact. When atoms on opposing surfaces were directly above and below each other, work of adhesion was lower because the hydrogenated surfaces could not come into as close proximity. The non-rotated tip used here does not suffer from this constraint. Figure 4 shows the contact patch while the tip is under 10 nN of load. The first two atomic layers of the silicon substrate, the surface hydrogen, and tip hydrogen atoms are shown in yellow, blue, and red, respectively. For visualization purposes, all tip Si and H outside of the contact zone are hidden. Close-up views of the cross section through the contact are shown in the insets of Fig. 4. Visualization of the full MD trajectory indicates that the apex of the tip translates laterally by a small amount so that the H at the tip apex settles into (111) FCC hollow sites on the surface (see Fig. 4a). Surface H atoms likewise fit into the opposing (111) FCC hollow sites on the tip apex. This tight interlocking of the tip and substrate results in lower potential energies and thus larger adhesive forces for the non-rotated case. There are two reasons why this may happen in Si, but was not observed in the previous simulations using diamond. First, a finite-sized silicon tip is more flexible than an infinite slab of diamond and allows for lateral accommodation. This effect may not be observed even with a finite-sized diamond tip due the fact that diamond is much stiffer than Si. Second, the (111) FCC hollow sites are larger for silicon simply because the lattice constant of Si is larger than diamond (0.543 nm vs. 0.3567 nm) [49]. When the tip is rotated 90° this interlocking is no longer possible due to lattice mismatch, as illustrated in Fig. 4b.

As briefly mentioned, the approximate work of adhesion \( W_{adh} \) for 100% terminated surfaces was calculated as

\[
W_{adh} = \frac{1}{A} \int F(r<0)dr
\]  

(2)

where the integral of the force \( F \) with respect to tip separation, \( r \), is carried out for the attractive portion of the loading curve (where \( F<0 \)) during separation of the tip from the substrate. For our calculation, the contact area \( A \) is estimated by the polygon inscribed by the red H atoms shown in Fig. 4, while the tip is loaded at 10 nN. Intermittent contact due to thermal fluctuations and change in area during the retraction process are thus ignored in this approximation. As noted earlier, this is an approximation and others have noted that this approach may not accurately predict the contact area [13, 51, 52]. This approach takes advantage of the fact that the \( N = 5 \) tips studied here are nearly flat at their ends, and the change in contact area during retraction is abrupt as it transitions from full contact to no contact. For comparison, we also use adhesive contact mechanics to determine the work of adhesion, although such models are based on continuum mechanics and thus ignore the atomistic details of the system. In fact, M.O. Robbins was one of the first to show that there can be a significant breakdown in these continuum
mechanics contact models at the atomic scale [12, 13]. By considering both approaches, we aim to provide reasonable estimates of the true value for \( W_{\text{adh}} \). From Eq 2, \( W_{\text{adh}} \) for the non-rotated and 90° rotated tips with 100% H-termination was calculated as 85 mJ/m² and 12 mJ/m², respectively. Using the continuum mechanics method of Grierson et al. [33], which treats the tips as rigid power-law profiles in the Derjaguin-Müller-Toporov limit [53], we obtain values of 85 mJ/m² and 45 mJ/m², respectively. The two methods agree well, particularly for the non-rotated tip.

The work of adhesion values are also reasonable when compared with other studies. In experimental studies, Ljungberg et al. [54] reported a range of surface energies between 12 and 20 mJ/m² for H-terminated Si (001). In that work, surfaces were treated in different concentrations of HF to remove the native oxide, which results in surfaces with a high degree of H-termination. For identical materials, the \( W_{\text{adh}} \) was taken as twice the surface energy, putting the range of \( W_{\text{adh}} \) reported by Ljungberg between 24 and 40 mJ/m². First principles calculations by Zhang et al. [55] have determined that the difference between H-Si (001) and H-Si (111) surfaces is less than 5%, with H-Si(111) having the lower surface energy. The experiments in Milne et al. [20], produced an average \( W_{\text{adh}} \) value of 8 mJ/m² for (111) oriented Si AFM probes. \( W_{\text{adh}} \) for the 90° rotated tips reported here falls within this range of experimentally measured values. \( W_{\text{adh}} \) for the non-rotated tip is well above the range of reported experimental values. However, the near perfect alignment of the crystal lattices between the tip and substrate for the non-rotated system makes it an extreme upper limit for \( W_{\text{adh}} \) that is unlikely to be observed experimentally due to the difficulty in making contact with the two surfaces in perfect alignment.

3.2 Adhesion in the Presence of Sliding

Milne et al. [20] showed that sliding of two Si tips increased adhesion relative to no sliding. The pull-off force measured was an average of 19 times higher with sliding, than without, and in some cases observations of adhesion forces after sliding that were 100’s of times larger than the average value obtained without sliding. The simulations presented here show similar results. The pull-off forces obtained after each sliding increment are plotted as a function of distance slid (Fig. 5a). For better statistics, the non-rotated and 90° rotated results have been averaged. The pull-off force tends to increase with increasing sliding distance as in experiment. Note that the magnitude of the increase is considerably smaller in the simulations, but so is the sliding distance (up to 10 nm in simulations vs. 10’s of nm to a few μm in the experiments), and the contact time (due to the much slower sliding speeds in the experiments). Thus, it is expected that the MD simulations would not produce increases in adhesion as large as those in the experiments. To consider this further, we performed an analysis comparing the trends in the work of adhesion values for the experiments and the simulations. We used the DMT theory to determine the work of adhesion values for the experiments (appropriate since the tips were reasonably fit with parabolic profiles), and the method of Grierson et al. [33] to estimate corresponding work of adhesion values for the simulations. Reassuringly, we find that there is reasonable, order-of-magnitude agreement between the experimental and simulation results. For all of the experiments, the work of adhesion values with sliding versus without increased by an average ratio of 30.6. For the simulations, we fit linear trendlines for work of adhesion versus sliding distance from least squares fits, and extrapolated to find the work of adhesion value at the mean sliding distance for all of the experiments. The resulting average increase in the work of adhesion depended on the H coverage, and was found to be 25, 15, and 12 for 80%, 90%, and 100% H coverage, respectively. Note that we compare to these high percentages of H coverage due to the fact that at 60% H coverage and below, tip wear seen in the simulations is far more significant than that seen in the experiments. Because the experimental results involved a range of randomly varied sliding distances, and different pairs of tips with different radii, we analyzed the experimental results further. Using a least squares fit, we determined the average percent increase in the work of adhesion per nm of sliding for all of the experimental measurements, and found the value to be 2.2% per nm of sliding. For comparison, in the simulations, the results are 2.2%, 1.2%, and 1.0% per nm of sliding for 80%, 90%, and 100% H coverage, respectively. This is reasonable agreement between the experiments and simulations; while it does not, in and of itself, fully validate that the simulation is capturing all essential mechanisms in the experiments, the consistency between them demonstrates that the interpretation of the experimental results based on the simulations is plausible.

The hypothesized mechanism for the increase in pull-off force seen in the experiments comes from removal of passivating species (e.g., hydrogen or hydroxyl groups) during sliding. The initial passivation was hypothesized to occur when fresh silicon surfaces were created in the experiments by removing the native oxide by fracture induced by contact and sliding; the bare silicon surfaces, when separated, then become exposed to the rarefied environment of the TEM, which nevertheless still hosts species such as hydrogen and water [56]. These and other species will dissociatively chemisorb onto the bare Si surfaces [57, 58]. Sliding disrupts this passivation and increases the likelihood of covalent bond formation. We observe wear in the form of displacement and transfer of atoms from one surface to the other including removal of H atoms and formation of Si–Si covalent bonds across the interface. In systems with the lowest hydrogen...
termination, the tips undergo the most wear while sliding, and have the largest number of covalent bonds between the tip and the surface just prior to pullback, which manifests itself as a large pull-off force. The effect of hydrogen termination on pull-off force is strong, with the two closely correlated (see Fig. 5b). The links between pull-off force and covalent bond formation are discussed further below.

The location of hydrogen atoms initially belonging to the tip and substrate can be tracked separately during the entire simulation. Examination of the atomic trajectories during sliding indicates that the tip picks up some hydrogen from the surface, and likewise deposits hydrogen back onto the surface at different points in the simulation. This exchange tends to favor removal of hydrogen from the tip and its deposition onto the substrate. An example atomic trajectory for the 50% H-terminated tip and substrate is shown in Fig. 6a. In this snapshot, the tip was slid from left to right for a distance of 5 nm. The tip was then retracted from the surface. The tip and substrate Si atoms are colored green and yellow, respectively, and the tip and substrate H atoms are colored blue and red, respectively, so that the transfer of material is apparent. The MD trajectories suggest that during sliding there is an initial removal of H from the tip when contact is first made, followed by transfer of Si from the tip to the substrate as sliding progresses, which results in tip wear. The net transfer of H atoms from the tip to the substrate as a function of H-termination is shown in Fig. 6b. It is clear that there is an increase in transfer of H from the tip to the substrate as sliding distance increases and that the rate of transfer generally increases with decreasing H-termination as long as there is H to be transferred. The maximum H transfer is at 40% H-termination.

Adhesion generally increases with more sliding. This is due, in part, to hydrogen removal which leads to the formation of interfacial Si–Si bonds between the tip and the substrate. This is apparent from Fig. 7. The pull-off force is shown in Fig. 7a as a function of the number of bonds in the contact just prior to pullback and the number of bonds as a function of sliding distance is shown in Fig. 7b). The H-terminations corresponding to each data set are given in

**Fig. 5**  
(a) Average pull-off force as a function of sliding distance and (b) Average pull-off force as a function of %H-termination. Data for non-rotated and 90° rotated tips have been averaged in both panels.
the legend. The values for the non-rotated and 90° rotated tips are averaged. Data sets for each tip alignment show the same trends with a bit more scatter. For systems with high H-termination few if any Si–Si interfacial bonds form regardless of sliding distance; however, pull-off forces up to approximately 100 nN are observed. This is, perhaps, indicative of the relative importance of the contributing factors governing the pull-off force, for example, the force to break the Si–Si bond and the force to overcome the van der Waals interaction. At low numbers of bonds, the van der Waals contribution contributes more to the overall pull-off force. As the number of Si–Si bonds between the tip and the substrate increase, the force to rupture these bonds begins to dominate the pull-off force.

It is also worth noting that although it is possible to increase the pull-off force with sliding distance for some systems, it is also possible to obtain small pull-off forces despite sliding 10.0 nm, for example. The low pull-off forces shown in Fig. 5 correspond to systems with large degrees of hydrogen termination where there is little wear and thus minimal Si–Si bond formation between the tip and the sample. In this case, van der Waals interactions dominate the pull-off force. When Si–Si interfacial bonds are formed, both the sliding distance and the H-termination, in addition to tip wear (discussed below) impact the pull-off force.

### 3.3 Reversible Adhesion

In experiments, the adhesion increase is observed to be reversible after separating the surface. As mentioned earlier, after sliding adhesion is high, with an average of 19× higher adhesion with sliding, than without. However, if adhesion is subsequently measured without sliding, with a lower bound of 5s delay between adhesion measurements, the original low adhesion values are recovered. Milne et al. [20] hypothesized that, in this interim time where tips are separated, the surfaces are repassivated with hydrogen or hydroxyl groups from the dissociative chemisorption of molecular hydrogen, water, or other trace contaminants in the TEM chamber, which lowers the adhesion [56–58]. Previous experiments have established that water and molecular hydrogen will indeed dissociatively chemisorb on clean Si surfaces. The repassivation process is beyond the time scale accessible to MD simulation so this hypothesis could not be tested directly. However, it is possible to replace the tips on artificially re-terminated substrates. After sliding 10.0 nm, 11 of the 14 tips were removed from the substrate and placed on a fresh substrate with hydrogen coverage that match the original tip termination. This is referred to as the “reset” condition. The 20% hydrogen non-rotated, 90° rotated tips, and 40% non-rotated tips were too severely worn after sliding to use any further so they were not included in this post-sliding analysis. These severely worn MD tips were also not used because the experiments of Milne et al. show minimal wear [20]. The simulated tips were then brought into contact with a fresh surface Si surface (with the hydrogen coverage still matching the original hydrogen coverage of the previous simulation run) and retracted once more using the same procedure used for the initial IHR simulations as described in Sect. 2. The results are shown in Fig. 8. In Fig. 8a, the initial pull-off force (no sliding) and the maximum pull-off force are taken from Figure 5a and replotted together. It is worth noting the maximum pull-off force may occur at different sliding distances depending on the hydrogen coverage, see for example Fig. 5b. That is, the maximum in the pull-off force does not always occur for longer sliding distances. While this is generally true for the lowest hydrogen terminations, where tip wear is greatest, the pull-off force is most strongly linked to the number of bonds in the contact prior to pull-off as shown in Fig. 7. The number of bonds in the contact prior to pull-off results from the interplay of tip wear.
wear, which is linked to hydrogen termination, sliding distance, and the stochastic nature of bond formation [21]. The relative change in the pull-off force with respect to the initial pull-off is plotted in Fig. 8b. After sliding, the adhesion increases considerably compared to the non-sliding case. When the previously used tips are placed on fresh surfaces, the adhesion recovers or in some cases is lower than the initial adhesion, where negative numbers indicate a decrease in adhesion relative to the initial value.

On average, the MD results reproduce the trend of the experiments, i.e., that a tip, after sliding and then separated from the opposing surface, will exhibit reduced adhesion when brought back into contact with a “refreshed” part of the opposing surface. In the simulations, no additional H atoms were added on to the tip, even though readesorption of passivating species will occur on both tip and surface in the experiment upon separation. Despite this, the recovery of low adhesion is still observed because the tip is interacting with an area of the surface unperturbed by sliding.

In some cases, adhesion is even lower after the “reset” than in the initial IHR simulations, most notably for the 40% and 50% H coverage. Fluctuations in the pull-off force values are not surprising given the stochastic nature of the bond formation events. Moreover, such variations are particularly unsurprising at low H coverage values, where more interfacial bond formation events occur due to the larger number of unsaturated Si bonds on the surface. They are also consistent with the distribution in adhesion values reported in the experiments [20]. Furthermore, the higher degree of roughness present on the tips after sliding, which is most prominent at lower H coverages, could also lead to variations in the adhesion force measured in the “reset” configuration. It is also plausible that frictional sliding creates a charge imbalance between the two bodies of silicon; however, the AFM tips used in the experimental studies (Mikromasch CSC37; Sofia, Bulgaria) were heavily n-doped, making the build-up of charge unlikely. This hypothesis was not considered in simulation.

Fig. 7 a Average pull-off force versus the number of bonds in the contact after sliding under 10.0 nN of load and at the time of pullback. b Average number of bonds as a function of sliding distance. Hydrogen termination is given in the legend. Data in both panels for non-rotated and rotated 90° tips at each distance and hydrogen termination are averaged.
An important contention of the passivation hypothesis, and our claim that these MD simulations are broadly supportive of it, is that conditions exist where relatively little wear occurs even though covalent bond formation and subsequent breakage has occurred. As mentioned above, the simulations do find that, at low H coverages, substantial wear and modification of the tip geometry can occur. However, much more modest wear occurs even though a sliding-induced increase of adhesion is observed, such as for 60%, 80%, and 90% initial hydrogen coverage levels. Testing the validity of this contention requires examining the atomic level structure of the tip surface in the experiments after sliding and separation has occurred. This was stated in our prior experimental report [20] but to further illustrate this, here we show an example where high-resolution TEM images with atomic resolution are obtained. Video 1 in the SI shows one such in situ TEM test of bare silicon sliding against bare silicon. The reversible adhesion phenomenon occurred in this case. In this video, the apex of the upper probe is magnified post contact, showing an extremely smooth and oxide-free Si surface with a high degree of order. Atomic features are seen, with roughness at the atomic level. This shows that atomic order and flatness is preserved, even though high adhesion attributed to covalent bond breaking has occurred, consistent with the MD simulations at intermediate hydrogen coverages. Nanoscale debris features are occasionally seen in the video; these are present at the edges of the sliding zone, and may either be from contaminants, or from accumulated Si atoms that have been displaced due to the mild wear process. Regardless, being at the edge and not within the sliding zone, it is assumed that these features do not have any primary influence on the adhesion behavior observed.

3.4 Friction and Wear

It has been shown both experimentally [30, 34, 35, 59–64] and using MD simulations that ordered substrates can display friction anisotropy and that, in the absence of wear, the friction traces display periodicity that is a direct result of the potential energy landscape encountered by the sliding tip/surface. These effects have been observed in MD simulations of the friction of diamond versus diamond [34, 36, 65], in ordered self-assembled monolayer surfaces [66–68], in MoS2 [69, 70], in carbon nanotubes [38], and in other systems [39, 71]. In the MD simulations presented here, these effects are present and will be reported elsewhere. Here, the focus is on changes in average friction and wear that occur as a function of sliding distance, hydrogen termination, and tip-substrate alignment when sliding in a fixed direction relative to the lower surface.

The average friction force during sliding as a function of sliding distance is shown in Fig. 9a and as a function of hydrogen coverage in Fig. 9b. Several aspects should be noted. First, for hydrogen terminations of 60% and lower, friction increases approximately linearly with sliding distance. The rate of increase is similar for 20–40% hydrogen terminations, but is larger than that for the 50–60% terminations. Second, the friction is independent of sliding distance for hydrogen terminations of 80% and higher. Insight into these differences can be gained by examining the net Si atom transfer between the tip and the flat surface as a function of sliding distance shown in Fig. 10a. For the 20 and 40% hydrogen terminations, the net Si atom loss is a nearly linear function of sliding distance, and smaller hydrogen terminations yield larger slopes. Thus, the linear increase in friction with distance for these low hydrogen terminations is largely driven by the formation of Si–Si covalent bonds between the tip and the substrate during sliding. Sliding introduces stress in these interfacial Si–Si bonds, which increases as the tip moves farther away from the bonding site on the surface. Eventually, stress induced by sliding is large enough to rupture these Si–Si linkages between the tip and the surface, while other times, the Si–Si linkage persists and a different Si–Si bond breaks within the tip, which results in the wear of the tips. This type of mechanism for...
breaking covalent bonds between surfaces was first observed in MD simulations by Harrison and Brenner [72]. In that work, two diamond surfaces with chemisorbed groups were in sliding contact. Hydrogen atoms were sheared from the chemisorbed groups. These free atoms were then able to extract hydrogen from the diamond surfaces creating a site for the formation of a covalent bond between the surface and the chemisorbed group to bond. Continued sliding caused the rupture of the carbon-carbon bonds between the chemisorbed group and the opposing surface, removal of the chemisorbed group from the diamond, and resulted in hydrocarbon debris between the surfaces. The wear of self-mated diamond contacts was later examined using MD and the REBO + S potential by Pastewka et al. They found that an amorphous layer of sp²-hybridized carbon forms during polishing and that the growth rate depends on the sliding direction [73]. Subsequent MD simulations have also observed the formation of covalent linkages between DLC surfaces sliding against diamond [74, 75] and against DLC surfaces [76–79]. For instance, Schall et al. examined the effects of unsaturated sites, i.e., hydrogen passivation, on the friction between DLC surfaces. Unsaturated carbon atoms served as initiation points for covalent-bond formation between the two surfaces, resulting in an increase in adhesion, and an increase in friction. The formation and breaking of covalent bonds at the interface during sliding resulted in material transfer and changes in hybridization of the carbon. Friction increased as the covalent linkages underwent strain and decreased when these bonds broke [76]. Quantum chemical simulations were used to examine the wear of diamond(110) in contact with silica. Those simulations show that bonding to silica chemically activates the C-C bonds in diamond, which leads to wear [80]. Tribocool reactions and tip wear have also been observed in MD simulations of Si tips in sliding contact with diamond [46, 81], DLC tips in sliding contact with both diamond [21] and DLC surfaces [82, 83]. Taken together these simulations have shown that unsaturated bonds in covalent materials, either present initially or

Fig. 9  Average friction as a function of sliding distance in a and versus hydrogen coverage in b. Data for the non-rotated and 90° rotated tips have been averaged.
formed during sliding, can lead to the formation of chemical linkages across the contacting interface.

The rate of Si atom removal, i.e., the slope in Fig. 10a, is markedly less for the 50% and 60% hydrogen terminations than for the 20 and 40% terminations. Fewer unsaturated sites are present initially and fewer are generated by sliding as evidenced by the reduced rate of hydrogen removal for these two hydrogen terminations compared to the 20 and 40% terminations (Fig. 6b). This reduction in the formation of covalent linkages between the tip and the substrate reduces the total friction force by reducing the component of friction arising from tip wear. Lastly, for the highest hydrogen terminations (80–100%) friction is low and independent of sliding distance. For these terminations, there very little wear (Fig. 10a and b), i.e., only one Si atom was removed from the tip, in the form of Si–H for highest hydrogen coverages. While a handful of hydrogen atoms are sheared from the tip at these high coverages, too few unsaturated sites exist on the tip and sample to facilitate the formation of interfacial Si–Si covalent bonds between the tip and substrate. Thus, the sliding distance has a little impact on friction (Fig. 9) because the tip is largely unchanged, i.e., unworn, and continually sliding over a pristine surface and energy is dissipated via stick-slip instabilities that result in the release of vibrational energy as phonons.

Archard’s wear law [84] states that the volume of material lost during sliding is proportional to the normal load and the sliding distance. While Archard’s phenomenological wear law holds for macroscopic contacts, it has been shown repeatedly to not apply to nanoscale contacts [85]. For example, atomic force microscope (AFM) studies have been used to study wear in covalent materials using Si tips sliding against diamond [24, 46]; DLC tips doped with Si sliding against silicon oxide [86] and ultrananocrystalline diamond [87]; silicon nitride against a variety of substrates [88]; DLC tips sliding against a DLC [89] surface; Si tips sliding on polymeric surfaces [90]. Archard’s law was not obeyed in any of these studies. Gotsmann and Lantz [90] observed that the rate of atom removal depended exponentially on stress and proposed that wear occurred via atom-by-atom attrition. This type of behavior was also observed for Si tips sliding against a diamond surface [24]. In contrast, atomistic simulations of tip-surface sliding have reproduced Archard’s law behavior, at least under some conditions [82, 83].

![Fig. 10](image1.png)

Fig. 10 a Average number of Si atoms transferred between the tip and the substrate versus the sliding distance. Hydrogen termination percentages on both the tip and the substrate are given in the legend. b Average total number of Si and H atoms transferred between the tip and the substrate as a function of hydrogen termination. Total tip sliding distance is given in the legend.

![Fig. 11](image2.png)

Fig. 11 The net number of interfacial Si–Si bonds between the tip and the substrate as a function of sliding distance for the non-rotated tips. Hydrogen coverages are shown in the legend. All coverages are shown in a and the higher coverages are shown in b.
83, 91]. For example, MD simulations of DLC tips sliding against DLC surfaces have shown that the number of atoms lost from the tip is linearly related to sliding distance for loads up to approximately 100nN. In addition, tip wear occurred via the loss of clusters that were worn from the trailing edge of the tip. Dai et al. [83] also carried out MD simulations of DLC tips sliding against DLC surfaces. They were able to recover Archard’s law under certain conditions and asserted that failure to recover the law could be attributed to a transition of the wear mechanism from isolated atom-by-atom wear to cluster-based wear of a blunted tip. Similarly, Shao et al. modeled DLC-diamond contacts, and observed a transition from atom-by-atom wear to Archard-like behavior at higher stresses [92].

Fig. 10a shows the number of Si atoms transferred from the tip to the surface, or worn, during sliding as a function of sliding distance. For hydrogen terminations of 60% and below, Archard’s wear law is obeyed in that a linear relationship between wear and sliding distance is observed. As noted above, the rate of atom removal is dependent upon hydrogen termination, increasing with decreasing hydrogen coverage, and thus the availability of unsaturated Si atoms that can form covalent bonds between the tip and the substrate. For large hydrogen terminations, there is very little wear. A more complete examination of whether Archard-like behavior is seen would require examining the load or stress dependence of wear, which is beyond the scope of the current work.

3.5 Wear Mechanisms

Wear of the tip was analyzed by plotting the instantaneous number of covalent bonds between the tip and the substrate as a function of sliding distance. The data for all hydrogen coverages of the non-rotated tips are shown in Fig 11. This plot makes clear the correlation between friction and the formation of tip-substrate covalent bonds. This correlation between friction and interfacial covalent bonds has been observed previously for DLC surfaces in sliding contact with diamond [74] and DLC [76] surfaces. The two hydrogen coverages with the highest friction, 20% and 40%, form bonds immediately upon contact with the substrate as is evidenced by the non-zero number of bonds at 0 nm (Fig. 11a). After approximately 1 nm of sliding, the number of bonds for the two lowest coverages increases dramatically with sliding distance. This is due to the wearing away of tip material and the exposure of a larger area of tip, which can then form bonds with the substrate. The transfer of material to the substrate and the evolution of the tip structure were analyzed by examining MD trajectories of the evolution of the apex of the tip during the course of the sliding. Figure 12 shows still images at the end of 10.0 nm of sliding from four simulations that used the non-rotated tip. Silicon atoms are colored according to their initial distance from the Si substrate, with red atoms being the closest. Hydrogen atoms are colored yellow. At the 20% hydrogen coverage (Fig. 12a), a few hydrogen atoms are transferred initially to the substrate. After about 1 nm of sliding, large sections of Si begin to be removed from the tip during sliding. The MD movies (Video 2, SI) also indicate that slipping, and wear, of an entire layer of Si atoms in the tip can occur.

Increasing the hydrogen coverage to 50% and then 60%, allows for the more gradual onset of wear as evidenced by the slower increase in the number of tip-substrate bonds as a function of distance for those hydrogen terminations (Fig. 11a). This reduction in interfacial bonds is concomitant with a reduction in friction for the 50% and 60% terminations compared to the lower H coverages. Analysis of the MD trajectory (Video 3, SI) reveals that the wear mechanism for the 50% hydrogen-terminated tip differs from the 20% terminated tip. In this case, the trajectories clearly show...
several individual hydrogen atoms removed from the tip prior to any loss of Si atoms. The majority of these hydrogen were originally located around the circumference of the contact patch, the point where the tip transitions from its flat apex to its curved shank. This is followed by the loss of two clusters of Si atoms, one Si$_8$H$_2$ and the second Si$_2$H, from the trailing edge of the tip. These clusters are evident at the far left of the snapshot in Fig. 12b. Continued sliding causes the loss of two additional multi-atom clusters. While material is lost from the trailing edge of the cluster, it is also clear that tip material can move through the contact from as far as the front third of the tip and eventually be removed. Removal of clusters of atoms from the trailing edge of the tip was also observed in MD simulations of DLC tips sliding on DLC substrates [82]. Comparison of the still images in Fig. 12a and b demonstrates that wear of the 50% hydrogen-terminated tip was significantly less than what was observed in the 20% terminated tip. For the 20% terminated tip, the tip layer that began closest to the substrate (red spheres) is almost entirely worn away, while much of this layer remains for the 50% terminated tip. Wear is further reduced with additional H-termination. Only Si small clusters are transferred after 10 nm of sliding (Fig. 12c) at 60% H-termination. Again, the wear process starts with the removal of H around the circumference of the contact patch, followed by the removal of small clusters of atoms (Fig. 12c). Above 80% H-termination, only a few H are transferred from tip to unsaturated Si sites on the substrate with little or no transfer of Si atoms and the number of bonds formed during sliding shows a very modest increase with time (Fig. 11b). In all cases, hydrogen is removed first from the outer circumferential edge of the contact patch (see for example Fig. 12d and Video 4, SI for the 90% H-terminated tip). In the case of the 100% H-terminated system, a single H atom was abstracted from the surface and deposited at the edge of contact. The removal or addition of H from or to the contact edges of the contact is likely the result of local structural disorder and local strains due to surface reconstruction, which lowers the energy barrier needed to remove the H or in the absence of H makes the tip edges more reactive. For high H-termination (>80%), even though hydrogen is removed during sliding there is still enough H present in the interface to provide separation between the tip and substrate and prevent covalent bonding between tip and substrate Si (Fig. 11b). Perhaps, with additional sliding, the continued removal of H from the tip could result in an increase in adhesion due to the exposure of unsaturated Si.

4 Summary and Conclusions

In summary, ReaxFF molecular dynamics simulations were used to study adhesion for silicon nanocontacts, specifically examining the dependence of adhesion on hydrogen coverage, relative orientation of the two Si crystalline surfaces in contact, and the degree of prior sliding. This work sheds light on the mechanisms of the reversible adhesion phenomena observed experimentally in Milne et al. [20] between passivated, oxide-free, nanoscale silicon surfaces in contact in vacuum. MD simulations presented here show that wear, adhesion, and friction, with and without sliding, depend strongly on the concentration of terminating hydrogen atoms, whether sliding occurred, and the formation of interfacial Si–Si bonds. In particular, lower hydrogen coverages and increased sliding lengths both lead generally to an increased number of interfacial Si–Si covalent bonds, which in turn increases adhesion markedly. The bond formation and breaking processes during sliding are stochastic, so fluctuations in the total number of bonds occurs, and the dependence of adhesion on sliding distance is not perfectly monotonic, but the general increasing trend is clear. Wear is present in the simulations and at low H-terminations, wear is severe. As H-termination increases, wear transitions from large clusters or complete layers of material, to small clusters, to the removal of H atoms, and eventually to a near wearless regime when there is complete H-termination. Moreover, after resetting the hydrogen termination post sliding (by making contact with a fresh portion of the surface) and then performing adhesion measurements without further sliding, it was observed in the simulations that adhesion returned on average to the relatively low values that were measured prior to sliding, mirroring the reversible adhesion phenomenon observed experimentally. A high-resolution TEM movie of one of the Si surfaces brought into contact in such an experiment reveals an extremely flat, well-ordered surface with roughness present only at the atomic scale. This is consistent with the simulations of surfaces at intermediate H coverage values, where sliding can increase adhesion while only slightly modifying the Si surface. In addition to providing a potential explanation for the reversible adhesion seen in Milne et al. [20], this work contributes to the growing body of tribochemistry work which explores the effects of energetic inputs, such as sliding and applied stress, on the chemistry at buried interfaces.

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