A fundamental mechanism for carbon-film lubricity identified by means of \textit{ab initio} molecular dynamics

Seiji Kajita$^{a,b,*}$, M. C. Righi$^{b,*}$

$^{a}$Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan
$^{b}$Istituto Nanoscienze, CNR-Consiglio Nazionale delle Ricerche, I-41125 Modena, Italy

Abstract

Different hypotheses have been proposed to explain the mechanism for the extremely low friction coefficient of carbon coatings and its undesired dependence on air humidity. A decisive atomistic insight is still lacking because of the difficulties in monitoring what actually happens at the buried sliding interface. Here we perform large-scale \textit{ab initio} molecular dynamics simulations of both undoped and silicon-doped carbon films sliding in the presence of water. We observe the tribologically-induced surface hydroxylation and subsequent formation of a thin film of water molecules bound to the OH-terminated surface by hydrogen bonds. The comparative analysis of silicon-incorporating and clean surfaces, suggests that this two-step process can be the key phenomenon to provide high slipperiness to the carbon coatings. The water layer is, in fact, expected to shelter the carbon surface from direct solid-on-solid contact and make any counter surface slide extremely easily on it. The present insight into the wettability of carbon-based films can be useful for designing new coatings for biomedical and energy-saving applications with environmental adaptability.

1. Introduction

Carbon-based films, as (poly)crystalline diamond and amorphous diamond like carbon (DLC), have attracted great interest from both the industry and

*Corresponding authors

Email addresses: fine-controller@mosk.tytlabs.co.jp (Seiji Kajita), mcrighi@unimore.it (M. C. Righi)
scientific community due to their exceptional physical, chemical, biomedical, mechanical and tribological properties.\[1, 2\] Tribologically, carbon films provide some of the lowest known friction and wear coefficients without any environmental pollution related to their use.\[3, 4, 5, 6\] However, the widespread application of carbon films has been hindered by a long-standing problem related to the influence of air humidity on their tribological performances.\[7, 8, 9, 10, 11, 12, 13, 14\] In DLC systems, for example, both highly positive and negative effects of humidity on the friction coefficients and wear rates have been reported even in the same type of tribological test conditions.\[11, 12\] This uncontrolled behavior is most likely the result of chemical reactions activated at the buried sliding interface interacting with water molecules. The chemical compositions of the carbon film and its hydrogen content can deeply alter the surface reactivity and friction.\[13, 14\] Indeed, friction reduction by moisture has been attributed to surface passivation by water chemisorption, which reduces the adhesion with a counter surface;\[9, 13, 15, 16, 17, 18, 19\] especially, hydrophilic hydroxyl groups are considered to play a crucial role in reducing the friction.\[9, 20, 21, 22\] In addition to the passivation, recent nano-scale experiments suggested another possible atomic mechanism to explain the extremely low friction of carbon-based film, which is connected to the presence of water molecules confined at the friction interface.\[10, 23, 24, 25\] By means of atomic force microscope (AFM) measurements it has been uncovered the presence of an adsorbed water layer, few molecules thick, which may function as boundary lubricant on DLC films.\[10\] A friction force measurement showed that the viscosity of the confined water layer is more than $10^8$ times greater than that of bulk water.\[23\] A nanoconfined water layer has been also considered to explain the lubrication mechanisms of steel by glycerol\[23, 26, 27\] and polymer brushes.\[28\]

The formation of a confined water layer seems favored by the incorporation of silicon atoms into the carbon matrix in a suitable dosing.\[29, 30, 31\] Si-doped DLC (Si-DLC) and SiC show, in fact, more stable and lower friction coefficients in water and humid environments than undoped DLC. Initially, the low friction mechanism of the Si incorporating carbon films was be-
lieved to be completely different from that of Si-free films and attributed to silica-sol wear debris resulting from the oxidation of silicon fragments by water vapor. However, films incorporating a low amount of silicon present very low friction in spite of the absence of any significant wear. Several authors have reported that water can dissociate directly at the silicon sites incorporated at the carbon surface leading to the formation of hydroxyl groups at these sites. By means of first principles calculations of water adsorption we showed that the hydroxyl termination enhances the surface hydrophilicity, in agreement with experimental observations. Kasuya et al. performed resonance shear measurements for evaluating the properties of water confined between silica surfaces with different concentrations of silanol (Si-OH) groups at the surface, and observed ice-like water on the surface terminated with a high concentration of Si-OH, which could provide lubricity under high normal pressure more than a low concentration of Si-OH groups. The formation of a structured water layer upon Si-OH termination of the carbon surface was also observed by classical molecular dynamics (MD) simulations.

Despite the growing interest in understanding the atomistic mechanisms for the low friction and wear of carbon-based coatings, our present understanding is limited by the difficulty in monitoring the buried sliding interface. A direct access by experiments is, in fact, extremely challenging and molecular dynamics simulations based on empirical force fields are typically inadequate for an accurate description of chemical reactions occurring in conditions of enhanced reactivity. Here we apply large-scale ab initio MD simulations that realistically describe the water/surface interaction, and provide in situ, real-time monitoring of tribochemistry processes. Thanks to a comparative study of Si-incorporating and pure diamond surfaces we highlight the pivotal role of the stress-assisted surface hydroxylation and the subsequent formation of a nano-confined layer of water molecules strongly bound to the surface.
2. Method

We perform \textit{ab initio} MD simulations based on the Car Parrinello method\cite{52} by means of the pseudopotential/plane-waves computer code included in the QUANTUM ESPRESSO package\cite{53}, which has been modified by our group in order to simulate tribological systems\cite{17}. Interfaces are modeled by periodic supercells of 15.1 Å × 10.1 Å × 20.0 Å dimensions, containing two diamond slabs 6 layers thick, with (6×4) in-plain size. The diamond surface presents a (2×1) reconstruction constituted of dimers that gives rise to alternating rows and trenches of sp²- and sp³-bonded carbon atoms. Bonds with this different hybridizations are also present in DLC\cite{54}, therefore our model aims at mimicking the local reactive sites of the DLC surface. The effects of larger-scale features, such as steric effects due to the roughness of DLC surfaces\cite{21}, are not taken into account in the present model. The large number of atoms included in our system (up to 378) and the simulated time intervals, about 10 ps for each trajectory, render our simulations computationally very demanding, in particular they required about 100 k cpu hours highly parallel supercomputers per each trajectory, which points out the importance and the complexity of the current work.

The electronic structure is calculated by means of the density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) approximation for the exchange correlation functional\cite{55}. The ionic species are described by ultrasoft pseudopotentials\cite{56}. The electronic wavefunctions are expanded in a plane-wave basis set with a cut-off energy of 25 Ry, and the Brillouin zone is sampled at the Gamma point.

In the CP dynamics, the ionic and electronic degrees of freedom evolve simultaneously, a fictitious mass of 450 a.u. is assigned to the electrons and the equations of motions are integrated with the Verlet algorithm with a time step of 5 a.u.=0.12 fs. Deuterium is used instead of hydrogen so as to avoid unphysical coupling between electronic and ionic degrees of freedom in the concurrent execution of the time evolution. The temperature of the system is kept constant
at 300 K by means of a Nosé-Hoover thermostat composed by double chains with frequencies of 30 THz and 15 THz.\textsuperscript{57, 58} An additional Nosé-Hoover thermostat is applied on the electronic degrees of freedom with frequency 200 THz. Mechanical stresses are applied along the [001] (load) and [110] (shear) directions. The water molecules (12 per supercell) are initially positioned in the configuration that we have identified as the most stable between the carbon slabs, and then the shear stresses and normal pressure are gradually applied adopting the same computational scheme as described in Refs.\textsuperscript{17, 59}.

3. Results

3.1. Tribologically-induced hydroxylation of the carbon film

We consider a sliding interface composed of a Si-incorporating C(001) surface partially hydrogenated and a fully hydrogenated H-C(001) countersurface. Si atoms are incorporated at substitutional dimer sites consistently with the experimental observation that silicon atoms in Si-DLC are surrounded by carbon atoms, and not by oxygen or other silicon atoms.\textsuperscript{61, 62} A density of Si atom corresponding to 8.3 % is realized, which corresponds to a typical dopant concentration in Si-DLC.\textsuperscript{33, 40, 38, 63} Figure 1 shows subsequent snapshots of the system dynamics under normal pressure of 5 GPa and shear stress of 1.25 GPa (the entire simulated trajectory is displayed in the movie of Supplemental data): after the onset of sliding, one of the substitutional Si atom captures a hydroxyl group from a confined water molecule, and a similar event happens immediately afterwards at another Si-sites. OH adsorption occurs also at unsaturated C-sites, but with lower frequency. To clarify the effect of Si doping, we repeat the simulations maintaining the same tribological conditions and interfacial hydrogen coverage, but without the incorporation of any Si atom. Figure 2 shows the number of adsorption events as a function of time for both the doped and undoped systems. The comparison of the results clearly indicates that the Si incorporation dramatically increases the reaction rate for water dissociative adsorption.
Figure 1: Snapshots (subsequent in time from left to right) acquired during the molecular dynamics simulation of a partially hydrogenated diamond interface incorporating Si-atoms under 5 GPa pressure and 1.5 GPa shear stress. The inset details the process of hydroxyl termination at one Si-site on the surface. The red and cyan balls indicate the O and H atoms of water molecules, respectively. The white color is used for the H atoms belonging to the initial interface termination.

Figure 2: Number of the adsorption events on the Si-doped and undoped surfaces during the dynamic simulations at 5 GPa normal pressure and 1.25 GPa shear stress. Each surface contains six unterminated sites. The closed and open circles indicate H and OH adsorption, respectively. The solid lines are guides for eyes.
Table 1: Distribution of the adsorbates attached to the initially clean Si and C surface sites at the end of six MD simulations 10 ps long. The simulations are carried out under normal pressure of 5 GPa and shear stresses of 1.25 GPa, 0.88 GPa and 0.0 GPa. Both Si-doped and undoped surfaces are considered.

|        | OH termination | H termination |
|--------|----------------|---------------|
| Si site| 34 %           | 10 %          |
| C site | 7 %            | 41 %          |

To verify the robustness of the result, we repeat the sliding simulation for both the systems of Fig. 2, but with different shear stresses of 1.25 GPa, 0.88 GPa and 0.0 GPa. The different adsorbate terminations of the surface sites observed during the simulations are reported in Table 1. The result shows that the Si sites present a probability to adsorb hydroxyl groups five time higher than the C sites, indicating that the Si dopants function as catalytic sites for hydroxylation.

The acceleration of the hydroxylation reaction by Si dopants observed in the dynamic simulations is consistent with our previous study based on static \textit{ab initio} calculations, which shows that the presence of Si dopants considerably decreases the energy barrier for water dissociation at the surface.\textsuperscript{45} Moreover, the analysis of the electronic charge displacements revealed that the larger polarization of Si-OH bonds with respect to C-OH bonds due to electronegativity differences, stabilizes hydroxyl adsorption at Si sites, in agreement with the distribution of the reaction products reported in Table 1. The present dynamics simulations, supported by the analysis of the energetics and thermodynamic stability of the surface termination,\textsuperscript{45} definitely prove that water dissociation is promoted by the Si-doping and hydroxylation most likely occurs at Si sites.

3.2. Formation and function of a water boundary layer

Having elucidated the mechanisms of surface hydroxylation in tribological conditions, we analyze the effects of this surface termination on the structure
and dynamics of the undissociated water molecules that remain confined at
the interface. To this aim we calculate the radial distribution functions (RDF)
for the O⋯H bonds shown in Fig. 3 (a). The RDF for bonds between the
water molecules and hydroxyl groups chemisorbed on the surface (green curve)
presents two peaks centered around 1.8 Å and 3.3 Å, which correspond to typical
hydrogen-bond distances between nearest and second nearest neighbor water
molecules, respectively.[64, 65] The RDF for surface-molecule bonds is, in fact,
very similar to that calculated for molecule-molecule bonds within the confined
water layer (blue curve). This similarity indicates that the adsorbed OH groups
participate to the hydrogen-bond network of the water film. In other words,
the Si-OH sites anchor water molecules by hydrogen-bonding and this link is
retained even in severe sliding conditions. On the contrary, the RDF profile
for the H-terminated surface shows the first peak located around 2.5 Å. This
longer bond distance indicates that the hydrogenated surface can not establish
hydrogen-bonds with the water molecules, which remain just weakly physisorbed
on it. The results of this analysis are confirmed by our previous static ab initio
calculations, which show that the physisorption energy of a water molecule is
three times lower in the presence of an adsorbed hydroxyl group than a hydrogen
atom.[45]

The hydrogen bond network established between the hydroxylated surface
and the confined water film affects the sliding dynamics of the latter. To clarify
this issue, we repeat the sliding simulation above described by changing the
amount of hydroxyl groups adsorbed on the lower surface, being the upper
surface fully hydrogenated and dragged with a force of same magnitude and
opposite direction. Figure 3 (b) shows the sliding distances covered by the
center of mass of the water boundary layer as a function of the sliding distance
of the lower surface, where the density of Si-OH groups ranges from 4.2 % upto
50 %. We can see that the water layer is dragged by the lower surface only
if the latter is hydroxylated, while in the case of fully hydrogenation (Si-OH
0 %), the confined water film fluctuates around its original position, without
any preferred direction. The higher the concentration of hydroxyl group at the
Figure 3: (a) Radial distribution function of the O⋯H bonds indicated by the arrows on the left side of the picture, where the ball-and-stick structures of the Si-incorporating surface (8.3 % Si-OH), water boundary layer, and hydrogenated countersurface are represented. (b) Sliding distance covered by the water boundary layer as a function of the distance covered by the Si-incorporating surface. Different concentrations of dopants are considered.
carbon surface, the more tightly the latter binds the water layer; e.g., the plot for the highest density of OH groups shows that the water layer slides coherently with the hydroxylated surface. Nevertheless, even in the low density case, 4.2% OH, the water molecules are attracted by the sliding surface.

Figure 4: Sliding distances for water layers confined between two surfaces containing the same amount of hydroxyl groups sliding in opposite directions. (a) The same simulation is repeated considering a fully hydrogenated countersurface. (b) The dynamic simulations are performed under 5 GPa normal pressure and 1.25 GPa shear stress.

We conclude by observing that a C-OH terminated-surface has a similar capability of water attraction as the Si-OH terminated one. This is elucidated by Fig. 4, which shows that doped and undoped surfaces containing the same amount of hydroxyl groups drag the water boundary layer with the same intensity. Indeed, the water layer remains almost at rest during the relative sliding of the two surfaces in opposite directions (panel a). On the contrary, the water boundary layer follows the C-OH surface if a fully hydrogenated counter-surface is considered (panel b), as it happened for the Si-OH terminated surface of Fig. 3(b).
4. Discussion

One of the proposed explanations for the low friction coefficient of DLC is that a graphite-like, sp² carbon tribolayer, generated by rubbing the film against a solid countersurface, decreases the interfacial shear strength. From this point of view, the mechanism of silicon doping in reducing the DLC friction is regarded as peculiar because it cannot conform to the above explanation; it is, in fact, well known that the silicon incorporation decreases the sp²/sp³ ratio of the carbon matrix. Therefore, researchers introduced another possible explanation for the observed friction reduction associating it to the transferred film of silicon-rich oxide often detected in spectroscopic analyses after the sliding tests. Since the oxides are formed in the presence of water vapor, it has been hypothesized that water hydrates the silicon-oxide wear debris and transform them in silica-sol, which may function as a sort of liquid-lubricant. The silica-sol mechanism was originally proposed to explain friction tests for SiC in water, during which silicon oxides, continuously generated and removed, form an extremely smooth, hydrated surface. However, the production of wear particles, as assumed by this mechanisms, not always takes place, as for example in films incorporating a low amount of Si dopants that provide low friction and wear simultaneously. Sen et al. performed friction tests to show that neither Si nor silica glasses exhibited lower friction than Si-DLC, and pointed out that the silicon element must be included within the amorphous carbon matrix to provide excellent frictional properties.

In parallel to the above observations, several authors have reported experimental evidences, such as derivatization X-ray photoelectron spectroscopy and nuclear magnetic resonance, that water directly reacts at the Si sites incorporated in DLC, producing Si-OH groups. Kato et al. identified a water layer of thickness ranging from 1 nm to 4 nm on the Si-DLC surface by using the spectroscopic ellipsometry, and proposed that this water layer lubricates the Si-DLC film. Recent resonance shear measurements revealed that the water confined between hydroxylated silica surfaces forms an ice-like structure that
increases the lubricity of the surface.\textsuperscript{148}

The present \textit{ab initio} MD simulations support the experimental observations pointing at the formation of a water layer that may function as a boundary lubricant. Figure 3 (b) indicates that even a small concentration of Si-OH, $\sim 4\%$, is able to attract water molecules and drag them during sliding. The effectiveness of a small dose of Si was also reported by experimental works, where the the friction reduction obtained by Si incorporation was observed up to a dopant concentration of 5 %.\textsuperscript{33, 38} The RDF analysis in Fig. 3 (a) reveals that relatively strong hydrogen bonds anchor the thin water layer to the hydroxylated surface. Thereby, it is reasonable to expect that the water boundary layer will not be easily squeezed out from the aperity contacts, preventing direct solid-on-solid contact and resulting in extremely low friction. On the contrary, the hydrogenated surface weakly attracts water molecules, which may be expelled from the interface in severe tribological conditions. This explanation is consistent with and can account for low-friction phenomena reported in previous studies.\textsuperscript{10, 23, 24, 26, 27, 42, 48, 49}

Our analysis suggests that the main role of Si dopants is to increase the density of hydroxyl groups at the surface by promoting its hydroxylation. This is supported by experiments reporting that a very small partial pressure of water, $10^{-3}$ Pa, is sufficient for the hydroxylation of Si-DLC,\textsuperscript{44} while undoped DLC loses their water adsorption capability at such low level of moisture.\textsuperscript{15}

In dry or hydrogen atmosphere, the H-terminated carbon films posses unmeasurably-low friction coefficient of about 0.01 or lower,\textsuperscript{9, 14} which originates from the smooth potential energy surfaces of the fully-passivated interface.\textsuperscript{18, 19} Surface passivation leads to extremely low adhesion and is able to keep the surfaces apart even under load, thus preventing the formation of covalent bonds and atomistic locking across the interface.\textsuperscript{3, 17, 18, 19, 68} In the case of atomically smooth surfaces, H-passivation has been found to be more effective than that passivation by water molecules.\textsuperscript{9, 14} Hydrogen bonding between the surfaces having the same hydroxyl termination can, in fact, increase the corrugation of the potential energy surface.\textsuperscript{9} The mechanism of surface hydroxylation fol-
lowed by the formation of a water boundary layer, which has been described in the previous section, provides a microscopic explanation for the observed increase of hydrophilic character of Si-doped DLC.[46, 47] An increase of surface wettability affects lubricity in many general situations, where for example the contacting surfaces have a different hydrophilic character and are not atomically smooth.[70]

A very important insight from our analysis is that the formation of a confined water layer triggered by the surface hydroxylation can be an universal friction mechanism for the extreme slipperiness of carbon films. Figure 4 indicates, in fact, that once hydroxylated, both undoped and Si-doped carbon surfaces display an identical capability of attracting water. This result is in agreement with recent AFM measurements for undoped DLC films that exhibit high lubricity in the presence of adsorbed water.[10, 23]

We conclude the discussion with a comment on experimental observations that show an increase of friction in Si-DLC at high levels of humidity.[35, 69] As stated above, a Si concentration of 5% has been proven to be sufficient to achieve low friction and the friction performance did not improve significantly by adding more Si dopants. If one performed a severe friction test of a densely-doped Si-DLC in high humid atmosphere, the wear would evolve considerably due to the silicon-rich oxidation and hydration, and the eroded surface would increase the friction coefficient during the test. Another possibility is related to the viscoelastic property of the confined water boundary layer. As pointed out by Sirghi et al., the effects of an adsorbed layer of water molecules is not always positive for the friction performance, because the water layer confined between surfaces terminated with highly-concentrated hydroxyl groups can form a condensed solid structure with higher shear stress.[10, 23] Indeed, amorphous solid water is well known to form several structures with different densities.[71, 72] In both the cases, the density of the hydroxyl groups is a key parameter to control the friction properties of the carbon-based films.
5. Conclusion

To elucidate the atomistic mechanism underlying the extreme lubricity of carbon-based films, we perform large scale \textit{ab initio} molecular dynamics simulations of sliding interfaces of both undoped and Si-doped diamonds interacting with water. We find that the Si dopants act as catalytic sites for surface hydroxylation. The adsorbed hydroxyl groups participate in the hydrogen bond network of molecular water confined at the interface, thus anchoring a thin water film to the surface. This two-step process well explains the enhancement of hydrophilicity observed upon doping DLC by silicon. The increased wettability most likely results in an increased lubricity of DLC coatings. On the basis of the observed sliding dynamics, we, indeed, expect that this water film is not easily squeezed out from contacting surfaces, preventing their solid-on-solid contact and making friction and wear very low. Interestingly, we show that pure carbon-based films once hydroxylated present the same capability of binding the nanoconfined water layer as Si-doped surfaces. The density of the hydroxyl groups is a key parameter to control the frictional properties in different environments. Since this parameter can be handled by suitable surface treatments\cite{48} and doping techniques,\cite{29,30,31} the results described in the present paper will provide important guidelines for carbon-material design in several fields related to energy-saving applications.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://
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The initial configurations are obtained by geometry optimization with static \textit{ab initio} calculations based on the density functional theory under 2.5 GPa normal pressure. The dynamic simulations start from the optimized configuration at 300K under 5 GPa normal pressure. The applied normal pressure is higher than typical Hertzian pressure, as we focused on the extreme conditions occurring at microasperity contacts, where the pressure can reach values of a few GPa. In this way we can monitor representative tribocorechemistry events, which happen on longer time scales under lower-pressure conditions, within the simulated time intervals of about 10 ps. The shear stress is applied gradually. In particular, the simulation initiates with 0.32 GPa shear stress that is held constant during the first 0.36 ps, then the shear stress is raised up with a 40 % increment every 0.18 ps until it reaches a value of achieves 1.25 GPa. The total time for the loading scheme is about $t = 1.1$ ps.

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