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## Predicting the hydrogen pressure to achieve ultralow friction at diamond and diamondlike carbon surfaces from first principles

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Hydrogen atmosphere can significantly change the tribological behavior at diamond and diamondlike carbon (DLC) surfaces and the friction-reducing effect depends on the partial pressure of hydrogen. We combined density functional theory modeling and thermodynamic quantities to predict the equilibrium partial pressures of hydrogen at temperature  $T$ ,  $P_{\text{H}_2}(T)$ , for a fully atomic hydrogen passivated diamond surface. Above the equilibrium  $P_{\text{H}_2}(T)$ , ultralow friction can be achieved at diamond and DLC surfaces. The calculation agrees well with friction tests at various testing conditions. We also show that  $P_{\text{H}_2}(T)$  increases with temperature; therefore, the temperature effect observed in friction tests should first be treated as an equilibrium factor rather than a kinetic factor. © 2008 American Institute of Physics. [DOI: 10.1063/1.2946661]

It is well known that lubricants can reduce friction. Recently, many researchers have found that testing atmospheres can significantly affect the tribological behavior of diamond or diamondlike carbon (DLC) coatings even in the absence of lubricants.<sup>1-6</sup> The coefficients of friction (COF) at diamond and DLC surfaces can drop from a high value (e.g., 0.5) to an ultralow value (e.g., 0.01) when the partial pressure of hydrogen  $P_{\text{H}_2}$  is increased.<sup>4-7</sup> Various experiments have confirmed that the lowest levels of friction and wear of diamond and DLC coatings can be achieved when the system is in a hydrogenous environment.<sup>2,4,5</sup>

The mechanism of friction reduction effect of hydrogen on diamond and DLC is attributed to the passivation of dangling bonds by the formation of C-H bonds, especially at two surfaces in sliding contact.<sup>2</sup> The modifications in the surface of DLC by the environmental atmospheres have been detected by x-ray photoelectron spectroscopy,<sup>8,9</sup> which shows more hydrogen stabilized  $sp^3$  carbon on the surface. The ground state molecular hydrogen can be thermotribocatalytically excited to efficiently passivate diamond surface during sliding.<sup>10</sup> First principles density functional theory (DFT) calculations<sup>11-13</sup> consolidated the understanding of hydrogen termination. For the  $\text{H}_2$  gas effect, Qi *et al.*<sup>13</sup> suggested that hydrogen dissociates and adsorbs on a diamond surface. Diamond surface reactivity results from sliding with Al such that the normally stable Pandey structure can deconstruct, thus exposing dangling bonds, and, making the surface more reactive with gas molecules.<sup>13</sup> The hydrogen passivation can totally change the direction of material transfer and largely inhibit adhesive transfer of Al to the diamond.<sup>12,13</sup> These modeling results qualitatively agree with the experimental observations.

Even though the mechanism of the reaction between hydrogen gas and diamond or DLC surface is well understood, both experiments and theoretical calculations are still qualitative. For example, although the dramatic changes in the COF on various carbon coatings have been observed by changing the partial pressure of hydrogen  $P_{\text{H}_2}$  and tempera-

ture  $T$ ,<sup>4-7</sup> a gap of  $P_{\text{H}_2}$  from  $10^{-3}$  Pa up to about  $10^2$  Pa has not been explored. In addition, none of the DFT calculations were able to reveal the effect of  $P_{\text{H}_2}(T)$  in friction tests. In this letter, we propose a new model that combines DFT calculations with thermodynamic properties to quantitatively predict the critical  $P_{\text{H}_2}(T)$  above which an ultralow COF can be achieved.

The main focus of this letter is to determine the relationship between hydrogen passivation to the dangling bonds and  $P_{\text{H}_2}(T)$ , based on the equilibrium state of the surface reaction. Although DLC is a complicated mixture in bulk, the local dangling bond and C-H bond topologies at a DLC surface are similar to various diamond surfaces.<sup>11,13</sup> Diamond surfaces with only one H atom per C atom, such as (111)- $1 \times 1$ :H and (100)- $2 \times 1$ :H, are more energetically stable.<sup>14,15</sup> Both surfaces have been observed typically in experiments<sup>16</sup> and used to mimic the diamond and DLC surfaces.<sup>11,13</sup> Similar trends in terms of reaction with  $\text{H}_2$  are expected for both surfaces. We adopt the diamond (111)- $1 \times 1$  for its lowest surface energy. We simplify the complicated tribochemical process into two static states: (1) contacting bare diamond surfaces with dangling bonds correspond to high friction and (2) fully hydrogen passivated diamond surfaces correspond to ultralow friction. We bridge these two states by the  $\text{H}_2$  reaction with the dangling bonds at the diamond surface. As with any chemical reaction, the direction of the reaction is very sensitive to  $P_{\text{H}_2}$  and  $T$ . Therefore, the tribochemical reactions at the diamond and DLC surfaces will change with environment and, in turn, affect friction and wear.

The diamond surfaces with and without hydrogen terminations are represented by the slab models, as in the Fig. 1 insets. Each slab contains six layers of diamond (111) planes, that is, 48 C atoms in total, with eight atoms at the two surfaces. When the two diamond surfaces are in contact without hydrogen, they form perfect crystal. The hydrogen dissociation at diamond (111)- $1 \times 1$  occurs via

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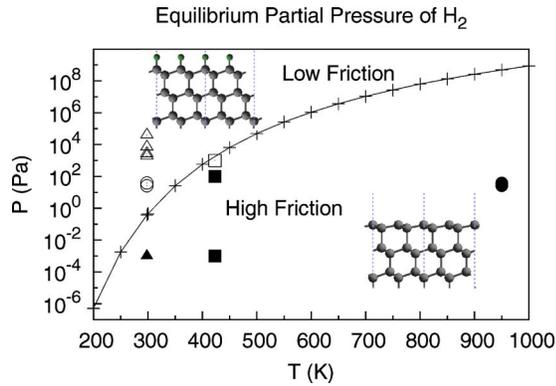


FIG. 1. (Color online) The equilibrium partial pressure of  $H_2$  to achieve a fully H passivated diamond (111) surface. The predicted high and low friction regions are marked, with the corresponding structures. Fully passivated diamond (111) and clean diamond (111)- $1 \times 1$  surfaces are shown at the upper and lower insets, respectively. H atoms are green, C atoms are gray. The filled symbols denote high friction (0.4), and the unfilled symbols denote low friction (0.1) observed in Refs. 5–7 and 10.



This reaction equilibrates at given  $H_2$  partial pressure  $P_{H_2}$ , and temperature,  $T$ , when

$$G_{(C-H)_8/C_{40}}(T) - G_{C_8/C_{40}}(T) = 4[\mu_{H_2}^0(T, p^0) + kT \ln P_{H_2}]. \quad (2)$$

Here  $G$  is Gibbs free energy,  $\mu$  is chemical potential,  $k$  is Boltzmann constant, and  $p^0$  is standard pressure (1 atm). The superscript 0 in Eq. (2) means the standard state in the thermodynamic sense.

The reference state used in thermodynamics is typically 25 °C and 1 atm, while in DFT it refers to 0 K and an isolated state. In order to derive the chemical potential from DFT calculations, a connection energy has to be defined to connect the two different reference states.<sup>17–19</sup> The connection energy at temperature  $T$ ,  $\Delta\mu^0(T)$ , stands for the difference of chemical potential between thermodynamics standard state and DFT 0 K reference state,

$$\Delta\mu^0(T) = \Delta\mu^0(T_r) + \int_{T_r}^T C_p dT - T \int_{T_r}^T C_p/T dT - (T - T_r)S^0(T_r). \quad (3)$$

Here  $\Delta\mu^0(T_r) = \int_{0K}^{T_r} C_p dT - T_r \int_{0K}^{T_r} C_p/T dT$  is the connection energy at room temperature ( $T_r$ ) under pressure  $p^0$ ,  $C_p$  is the molar heat capacity at constant pressure, and  $S$  is the entropy. Through  $\Delta\mu^0(T)$  we can derive chemical potentials at finite temperatures from DFT 0 K energy calculations and available thermodynamics data.

For a solid, the effect of pressure can be ignored,<sup>17</sup> and hence the connection energy can be integrated from 0 K to  $T_r$ . For a gas, the connection energy must be calculated from an equilibrium reaction involving a reference solid.<sup>17–19</sup> For  $H_2$ , we choose LiH since thermochemical data for both Li and LiH are readily available. The connection energy for  $H_2$  gas is

$$\Delta\mu_{H_2}^0(T_r) = 2[\Delta H_{LiH}^0(0 K) - \Delta G_{LiH}^0(T_r) + \Delta\mu_{LiH}^0(T_r) - \Delta\mu_{Li}^0(T_r)], \quad (4)$$

where  $\Delta H_{LiH}^0(0 K)$  is the formation energy calculated from DFT for 0 K,  $\Delta G_{LiH}^0(T_r)$  is the standard Gibbs formation energy at room temperature. For the formation energy calcu-

TABLE I. Computed  $\Delta\mu^0(T_r)$  for Li, LiH, and  $H_2$  and related quantities from handbook.<sup>35</sup>

	$H^0(T_r) - H^0(0 K)$ (kJ/mol)	$S^0(T_r)$ [J/(mol K)]	$\Delta_r G^0(T_r)$ (kJ/mol)	$\Delta\mu^0(T_r)$ (eV)
Li	4.631 <sup>a</sup>	29.140 <sup>a</sup>	-	-0.0421
LiH	0.378 <sup>a</sup>	20.021 <sup>a</sup>	-68.4 <sup>a</sup>	-0.0579
$H_2$	-	31.208 <sup>a</sup>	-	-0.368

<sup>a</sup>Ref. 35.

lation, VASP<sup>20,21</sup> in conjunction with PAW potentials and GGA<sup>22,23</sup> were used for LiH,<sup>24</sup> diamond slabs, and  $H_2$ .<sup>12</sup> The calculation results, together with the essential data required for the calculation, are listed in Table I.

The  $C_p$  formula for temperatures above  $T_r$  is taken from Ref. 25 as  $C_p(T) = 27.37 + 3.33 \times 10^{-3} T$  [in J/(mol K)]. For temperatures from 200 K up to  $T_r$ , it is fitted to data tabulated in Ref. 26 as  $C_p(T) = 19.93 + 5.334 \times 10^{-2} T - 7.867 \times 10^{-5} T^2$  [in J/(mol K)].

Equation (2) can now be rewritten with the connection energy calculated for  $H_2$  and ignoring the temperature dependence<sup>17</sup> of  $G_{(C-H)_8/C_{40}}(T) - G_{C_8/C_{40}}(T)$ ,

$$kT \ln P_{H_2} = \frac{1}{4} \Delta H - \Delta\mu_{H_2}^0(T), \quad (5)$$

where  $\Delta H$  is the change in enthalpy of reaction (1) at 0 K, which was computed to be -2.754 eV from DFT calculations, based on the details listed in Refs. 12 and 27.

Figure 1 shows the calculated equilibrium partial pressures of  $H_2$  for the reaction (1) at temperatures ranging from 200 to 1000 K via Eq. (5). At a given temperature, when  $P_{H_2}$  is above the equilibrium pressure, a fully passivated diamond/DLC surface is favored, thus a low or ultralow friction is anticipated. When  $P_{H_2}$  is below the equilibrium pressure, the atomic hydrogen at the diamond/DLC surface will desorb from the surface, resulting in impassivated dangling bonds and high friction. As Fig. 1 shows, the equilibrium partial pressure increases with temperature. This means that more hydrogen is needed to maintain the hydrogen coverage on a diamond surface at higher temperatures. Therefore, ultralow friction can be achieved with a fully H-passivated diamond or DLC surface, by either increasing  $P_{H_2}$  or reducing  $T$ .

The equilibrium pressure  $P_{H_2}(T)$  divides the testing environment (partial pressure and temperature) in Fig. 1 into low or ultrahigh friction and high friction regions. Dramatic changes in frictional properties are observed when the testing conditions vary from one region to the other. These experiments are now summarized in Fig. 1. The agreement of these experiments with the present model is excellent.

Konca *et al.* tested friction of an aluminum pin sliding against nonhydrogenated DLC at room temperature.<sup>5</sup> The DLC surface was originally in the high friction region. The observed COF reached 0.8 when  $P_{H_2}$  fell below  $0.4 \times 10^{-3}$  Pa, while an ultralow COF about 0.015 was observed when  $P_{H_2}$  exceeded  $1.88 \times 10^3$  Pa. The change in  $P_{H_2}$  from  $1.88 \times 10^3$  to  $40.52 \times 10^3$  Pa only changed the time to achieve ultralow friction. These experimental results agree well with the calculated equilibrium partial pressure 0.38 Pa at room temperature.

Room temperature friction tests of CVD diamond on diamond reported by Feng *et al.*<sup>4</sup> showed high friction

(0.6–1.0) in UHV and low pressure of  $1.0 \times 10^{-3}$  Pa, both below the calculated equilibrium  $P_{\text{H}_2}$  of 0.38 Pa. Although the CVD diamond surface was naturally passivated by atomic hydrogen,<sup>13</sup> the desorption of hydrogen eventually resulted in high friction under the low partial pressure of hydrogen at room temperature.<sup>4</sup> In friction tests of a diamond tip sliding on polycrystalline CVD diamond films in UHV at room temperature, Perry *et al.* found that the COF is 0.6–0.8, varying with the content of amorphous carbon phase.<sup>28</sup> Gardos and Gabelich performed friction tests on polycrystalline diamond (100) surfaces with varying temperatures from  $T_r$  to about 900 °C with 13–39 Pa  $\text{H}_2$ , and observed friction increasing with temperature for all  $P_{\text{H}_2}$  tested.<sup>10</sup> Large variations existed in these experiments, due to the difference between measured temperature and the true surface temperature or the sequences of sliding tests. Eventually, high friction was consistently reached after several passes at the same track at the peak temperature,<sup>10,29</sup> suggesting that high friction may be the equilibrium state at about 700 °C. Nevertheless, the low COF at room temperature and the trend of increasing COF with increasing temperature are in agreement with our model.

The hydrogenated DLC film (with a hydrogen content of 34 at. %) tested by Fontaine *et al.*<sup>6,7</sup> can be considered as an initially passivated surface with low friction. High COFs were observed both under UHV and low COFs under  $1.0 \times 10^3$  Pa  $P_{\text{H}_2}$  at room temperature,<sup>6,7</sup> both agreed well with the present calculations that  $P_{\text{H}_2}$  (300 K)=0.38 Pa. At 150 °C, high COFs were observed under UHV and  $0.1 \times 10^3$  Pa, while low COFs were found under  $1.0 \times 10^3$  Pa,<sup>6,7</sup> which is slightly lower than the calculated  $P_{\text{H}_2}$  of  $1.9 \times 10^3$  Pa at 150 °C. The DLC film in their friction tests contains 34 at. % hydrogen, while we assume in our model that the hydrogen flux only between the ambient atmosphere and the diamond surface, but not through the coating to the surface. The supply of atomic hydrogen from the coating itself will reduce the partial pressure needed to achieve hydrogen passivation at the DLC surface. Hydrogen reservoirs can also be made by hydrogen-containing DLC or Ti subsurface layer, which significantly reduces the friction as the atmosphere containing hydrogen.<sup>30</sup> For the hydrogenated DLC, decreasing hydrogen content has been detected during wear tests in air at room temperature.<sup>31</sup> Those confirm that the tribochemical desorption of hydrogen occur when  $P_{\text{H}_2}$ , which is nearly zero in air, is below the equilibrium value.

Fontaine *et al.* have considered temperature as a kinetic factor that affects the time needed to reach steady friction stage.<sup>7</sup> As we see from most of the friction tests, the temperature did not affect the final COFs,<sup>6,7</sup> even in the tests that involved suspensions and restarts of sliding.<sup>4,5</sup> This indicated that an equilibrium state had been reached after complicated tribochemical reactions involving material transfer occurred. Based on the dramatic change in the  $P_{\text{H}_2}$  due to the temperature in the present calculation, the temperature effect in the friction tests under  $\text{H}_2$  environment should first be considered as an equilibrium factor. If the diamond or DLC film has already been fully passivated by hydrogen, further lowering the temperature (just as further increasing  $P_{\text{H}_2}$ ) will not correspondingly further lower COF.

The general agreement with experimental results on DLC and diamond coatings validates the rather idealized model. Errors can come from the diamond (111)- $1 \times 1$  sur-

face assumption. As we know that DLC is a mixture of  $sp^2$  and  $sp^3$  bonded carbon atoms and the diamond coatings can be (100) or (111) orientated, the entropy of the surface reaction should slightly deviate from the ideal (111) surface. Therefore the equilibrium partial pressure should become a broadened region. Friction is more complicated with applied load, contact area, sliding speed, and sliding directions *et al.*,<sup>32,33</sup> some of which have been modeled by large scale molecular dynamics simulations and directly compared with experiments.<sup>34</sup> They also influence the tribochemistry. Increasing contact area might reduce the amount of dangling bonds formed in friction due to less contact pressure, thus decreasing friction. Increasing sliding speed might lead to insufficient time for hydrogen dissociation, thus resulting in high friction. These conditions need to be considered to refine the tribochemistry model in future work.

In summary, we calculated  $P_{\text{H}_2}(T)$  for a fully passivated diamond (111)- $1 \times 1$  surface. The calculation agrees well with friction tests on both diamond and DLC coatings at various testing conditions. The calculation results show that  $P_{\text{H}_2}$  increases with temperature. Therefore, the temperature effect observed in friction tests should first be treated as an equilibrium factor rather than a kinetic factor. The results also suggest guidelines for the design of low friction diamond and DLC coating surfaces for tribological applications.

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