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Comparative study of friction properties for hydrogen- and fluorine-modified diamond surfaces: A first-principles investigation

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ABSTRACT

The van der Waals corrected first-principles approach within density functional theory has been performed to calculate the interaction energies and friction coefficients for hydrogen- and fluorine-terminated diamond film systems. Comparative studies show that the fluorine-terminated diamond film is more stable and chemically inert than that of hydrogen termination. The repulsive interactions between two fluorine-terminated diamond films are stronger than that of hydrogen termination system, and the former system has a larger equilibrium adsorption heights than that of the latter. Quantitative calculations show that the hydrogen-terminated diamond film system has larger potential barriers and hence larger friction coefficients of about 0.15 under the loads of 0.5–3 nN, which are almost twice larger than that of fluorine-terminated system (about 0.08). The results are in good agreement with experiments and other theoretical predictions.

1. Introduction

Diamond-like carbon (DLC) film, as one of the most promising solid-state lubricant, has been applied to reduce friction and wear of interface in micro machines and micro electrical mechanical systems, because of its high hardness, wear resistance, chemical inertness, and low friction coefficients [1]. The unique frictional behaviors of DLC film are affected by many factors such as chemical and structural natures, substrate and counter face of material, contact pressure, motion speed and test environment, and thus the tested friction coefficients of DLC films span a wide range of 0.001–0.7 [2]. Therefore, understanding the disparity of the friction coefficients of DLC films at atomic scale has become a hot research area. Artificially grown by chemical vapor deposition, hydrogen (H) is present in processes; thus DLC films obtained by this method are usually H terminated [3]. A number of experimental studies confirm that the formation of a highly H-terminated surface has little chemical and physical interactions between sliding DLC films, and plays a crucial role in low levels of friction and wear [4–7]. Compared to H-terminated DLC film, experiments show that fluorine (F) terminated DLC film has lower friction coefficients, wear and higher hardness [8,9]. As a kind of special coating material, F-terminated DLC film has been applied to bearing surface and hard facing widely, with a vastly improved reliability and longevity of mechanical engagement. Therefore, understanding of the different friction characters between H- and F-terminated DLC films is important and interesting in both theory and practical applications.

Computation simulation is a kind of powerful method to understand the mechanism of microscopic friction behaviors. Using classical molecular dynamics method, several researchers have proved that the H atom bonded to DLC film can reduce friction and wear [10–13]. Compared with classical dynamics method, first-principles calculations are more accurate in handling the electronic structures. Based on the first-principles calculations, a number of studies have been conducted on the friction characters of H-terminated DLC film [14–16]. However, most of the researches focused on the situation of free load, and only provided a qualitative explanation. The only quantitative calculations of the friction properties for H- and F-terminated diamond (111) surfaces were carried out by Neitola and Pakkanen using quantum chemistry method [17,18]. However, their results showed that the friction coefficients of the H-terminated diamond (111) surface system are smaller than that of F-terminated system, which is in contradiction to experiments and other theoretical predictions [8,9,19]. Therefore, understanding of the different friction properties between H- and F-terminated DLC films is still insufficient. The further detailed studies of the friction properties of the two kinds of films are needed.

The aim of this research is to quantitatively investigate the friction difference between H- and F-terminated DLC film systems. Using more accurate periodic model, we applied first-principles calculations based on density function theory (DFT) to calculate the interaction energies and friction coefficients for H- and F-terminated DLC films by the method of Zhong and co-workers [20–22]. Our comparative

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investigations are in good agreement with experiments and other theoretical predictions. The results of this study may be beneficial to researchers in better understanding the effects of termination on interface friction properties.

2. Model and computational method

All our calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code [23,24], equipped with the projector augmented-wave (PAW) method for electro-ion interaction [25,26]. The wave functions were expanded in a plane-wave basis with an energy cutoff of 480 eV. The exchange–correlation interaction was treated with the generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE) [27]. Dispersion interactions are very important for our calculation. However, standard DFT method fails to describe the long-range dispersion interactions exactly. Therefore, the semiempirical DFT-D2 Grimme's method that has brought satisfactory investigations in previous studies was employed to calculate the dispersion interactions [28–31]. Standard values for the dispersion coefficient C_6 (1.75, 0.14 and 0.75), vdW radii (1.452, 1.001 and 1.287) for C, H and F atoms were used, respectively.

We considered the more easily cleaved (111) surface of diamond, with its dangling bonds saturated by H or F atoms, respectively. For the situation of fully H-terminated diamond (111) surface, the most stable structure is the dereconstructed (1×1) (H–C (111)) surface, with H atom on top of C atom [32]. To compare with H–C (111), full F-terminated diamond (1×1) (F–C (111)) surface was also chosen. The slab thickness of the calculated model includes eight C layers and two termination layers (the back side of the slab was also terminated by H atom). The friction systems were constructed by the two above slabs facing each other in the same cell.

The irreducible Brillouin zone integration was carried out by using the $15\times15\times1$ Monkhorst–Pack grids for our models [33]. The total energy was converged up to 10^{-4} eV for electronic structure relaxations. For geometry optimizations, all the internal coordinates were relaxed until the Hellmann–Feynman forces were less than 0.02 eV/Å. A vacuum layer at least 15 Å was set to avoid the interactions between the adjacent images for all systems.

3. Results and discussion

The optimized lattice parameter of bulk diamond is 3.57 Å, which is in good agreement with experimental and theoretical values [19,34]. The full structural relaxations of the H–C (111) and F–C (111) films were performed and the optimized structures are shown in Fig. 1. The C—H bond length of 1.11 Å is slightly shorter than that of C—F (1.38 Å). The influence of the adsorbates on substrate geometry has also been examined. We find that the interlayer relaxations for H– and F–C (111) films have the same tendencies, and the relaxations are almost located at the first interlayer space, with contractions of 5.1% and 2.4% for H and F terminations, respectively. Fig. 1(c) and (d) shows the charge density differences induced by the terminations of H and F atoms. Because of large electronegativity difference between H and H atoms, the C—H bond represents highly covalent bond character with charge gathered between them, but the C—F bond is of ionic bond character with the obvious charge transfer from C to F atoms. The energy needed to take away an H atom from the H–C (111) film is 4.75 eV, which is smaller than that of taking away an F atom from F–C (111) film (4.95 eV). These results indicate that the F–C (111) and H–C (111) films have different surface electron structures.

On the basis of the optimized films, we constructed the interface sliding models, as shown in Fig. 2. The two films are placed facing

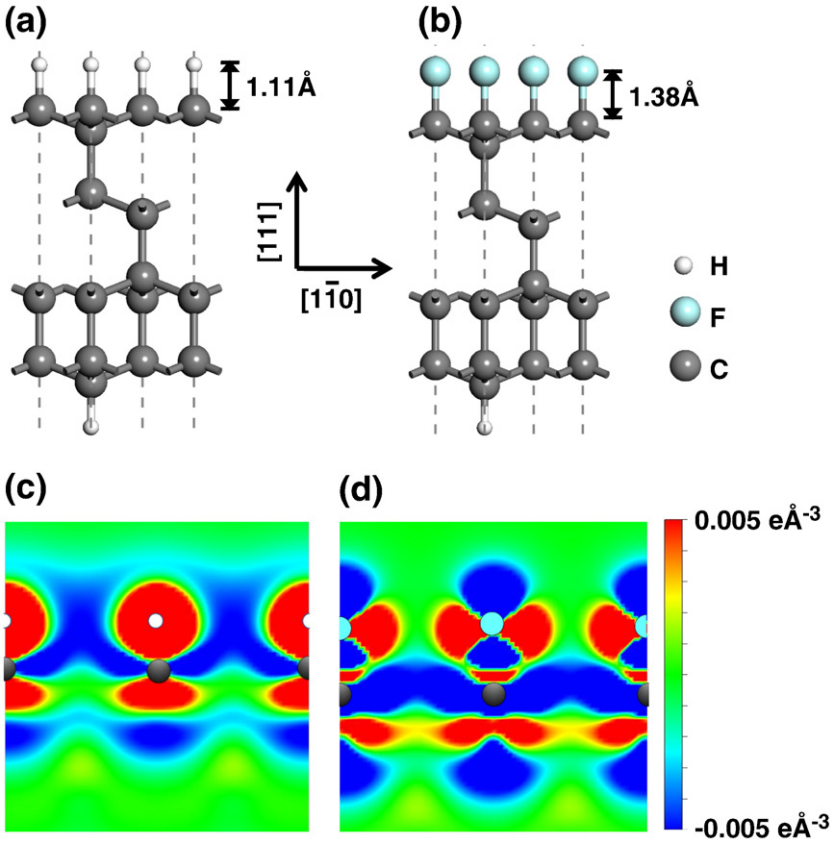

Fig. 1. Optimized geometry structures of (a) H- and (b) F-terminated diamond (111) films, and the corresponding electron density differences are shown in (c) and (d), respectively.