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An atomic scale study of ultralow friction between phosphorus-doped nanocrystalline diamond films

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ABSTRACT

The van der Waals corrected first-principles approach within density functional theory was used to investigate the nanofriction properties of phosphorus-doped nanocrystalline diamond films. Our results demonstrate that substitutional phosphorus atoms can significantly decrease the coefficient of friction between two hydrogenated diamond films, and the doping effects are affected by the interfacial environment. These nanofriction modulations can be elucidated by interfacial charge redistribution induced by doping atoms. Our study presents an electronic level mechanism of the doping effects on friction properties of doped interfaces.

1. Introduction

The exceptional properties of ultra-smooth nanocrystalline diamond (NCD) films make them a suitable structural material for micro- and nano-electromechanical systems (MEMS/NEMS); such properties include smooth surface, high stiffness, excellent chemical inertness, good wear resistance and low coefficients of friction (COF) [1–3]. The tribological behavior of NCD films significantly varies from one type to another, and the tested COF of diamond films ranges from 0.001 to 0.7 because of the effect of film qualities and test conditions [1]. Therefore, elucidating the friction differences of different NCD films have attracted considerable attention.

Interfacial environment and inner structure are the two major factors that affect tribological behaviors. Consequently, 'friction-induced graphitization' and surface passivation have been postulated as the two well-known mechanisms for the lubrication of carbon based films [4–16]. However, which one is the primary lubrication mechanism is still being debated. Extensive theoretical and experimental investigations have revealed that interfacial environment is important in determining the friction properties of diamondlike carbon (DLC) films [4–14]. Surface passivation is an important mechanism of the interfacial environment effect on friction. For example, the hydrogen (H), OH and O fragments resulting from the dissociative adsorption of H_2O and O_2 molecules can saturate dangling bonds of NCD films to maintain the films as distant from one another and decrease the resistance against sliding [6,9]. Recently, Wang's studies provided further evidences to support the passivation mechanism that passivation of carbon dangling bonds at the sliding interface plays a critical role in determining the lubrication of DLC films [13,14]. The inner structure exhibits more complicated effect on friction properties than that of the interfacial environment. The type and ration of bonds (i.e., sp^2 and sp^3) can affect the mechanical and tribological properties of DLC films. DLC films with more sp^2-bonded carbons are relatively soft and exhibit similar tribological performance to that of graphite, whereas the films with high proportion of sp^3-bonded carbons are similar to diamond; hence, the latter films are very hard and provide superior friction properties [12]. Experimental and theoretical studies have shown that 'friction-induced graphitization' is a viable and important lubrication mechanism [15,16].

Dopant is a general structure defect that can effectively change the electrical and geometrical structures of the diamond material. The effects caused by incorporation of dopant atoms, such as boron (B), phosphorus (P), and sulfur in chemical vapor deposition (CVD) DLC films have been widely investigated. Most studies focused on the influence of doping on the structures and growth behaviors, whereas the effects of doping on the tribological properties of DLC films have been rarely investigated, particularly for NCD films [17–20]. B is one of the most prominent impurities

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in NCD films because B atoms can be readily incorporated into the diamond lattice and form a p-type semiconductor with tunable electrical conductivity. Liang et al. and Wang et al. separately reported the decreased friction of B-doped NCD films [21,22]. Preparation n-type doped NCD films are quite difficult compared with p-type doped NCD films because the impurity levels of the former are relatively deep and the electrical resistivity is very high; thus, the technical requirements of the semiconductor electronic devices are not satisfied. P is the most promising n-type doping element. The n-type diamond has already been fabricated on (111)- and (100)-oriented diamond through gas-phase P doping during a plasma-enhanced CVD process [23,24]. The electronic structures and the carrier transport of P-doped NCD films have been theoretically and experimentally investigated [25,26]. These studies revealed that the electronic structures and electron conductivity of NCD films could be improved by introducing P atoms. Our previous studies confirmed that electronic structure is one of the most important factors for the differences in friction behaviors [11,27,28]. Therefore, P-doped NCD films are expected to exhibit different tribological characteristics from that of the undoped system. However, to our knowledge, investigations on the friction of P-doped NCD films is still lacking in the published literature. Therefore, elucidating the tribological properties of P-doped NCD films is important to broaden their application in MEMS/NEMS.

In this paper, we performed density functional theory (DFT) calculation, which is more accurate in handling electronic structures to determine the effects of substitutional P atom on the friction of NCD films at the atomic scale. One major finding of this work is that P atom doping can dramatically decrease the nanoscale friction between NCD films because of the redistribution of interfacial electrons. This result can be helpful in understanding the nanoscale friction of doped diamond films.

2. Methodology

DFT is an effective method to investigate the electronic structures and interfacial interactions. Vienna Ab-initio Simulation Package (VASP) code equipped with the projector augmented-wave (PAW) method for electron–ion interactions was employed to our calculations [29–31]. We treated the exchange–correlation interactions with the generalized gradient approximation (GGA) in Perdew, Burke, and Ernzerh (PBE) parameterization [32]. For fully H atom passivated NCD film, the strong covalent bonding at sliding interfaces is shield by terminated H layer. Thus, the long range nonbonding attractions, such as electrostatic, polarization and vdW interactions start to play a more and more determining role in interfacial properties [4]. The semiempirical DFT-D2 approach of Grimme, which has brought reasonable investigations in various systems, was employed to describe the vdW interactions between two NCD films. Standard values for the dispersion coefficient C6 (1.75, 0.14 and 7.84), vdW radii (1.452, 1.001 and 1.705) for C, H and P atoms were used, respectively [33]. The optimized lattice parameter for the bulk diamond is 3.57 Å, in good with experiments. We used $(9\times9\times1)$ Monkhorst-Pack grids to sample the two-dimensional Brillouin-Zone [34]. The wave function was expanded in a plane-wave basis with an energy cutoff of 500 eV. The total energy was converged up to 10^{-4} eV for electronic structure relaxations. A vacuum layer of at least 15 Å was set to avoid the interactions between the adjacent images. We adopted the procedure of Zhong et al. [35], which has successfully calculated graphene and diamond systems [11,27,28,36], to calculate the nanofriction properties.

Although NCD films possess complicated mixture, the local dangling and carbon–hydrogen (C–H) bond topologies at the films

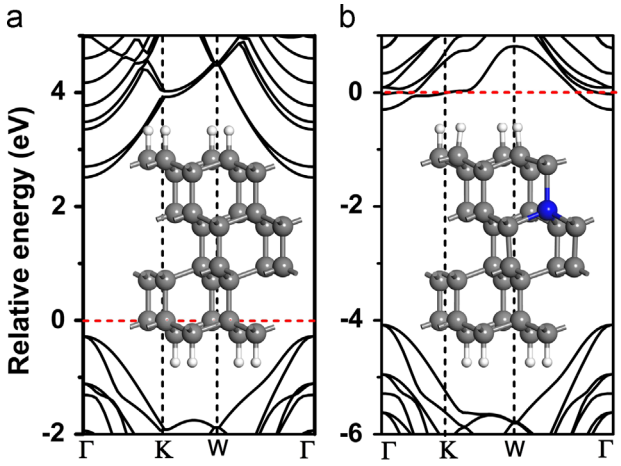

Fig. 1. Optimized geometry and band structures of (a) undoped and (b) P-doped H–C (111) film. The red-dashed lines represent the Fermi energies. Blue, gray and small spheres represent P, C and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are similar to different diamond surfaces [37]. H-terminated diamond (111)-(1×1) surface, with one H bonded to one C, has been achieved in experiments and used to simulate DLC films [37,38]. In our calculations, a (2×2) supercell of H-terminated diamond (111) surface [H–C (111)] was used to mimic an undoped NCD film, as shown in Fig. 1(a); the supercell contains eight C layers and two H termination layers (total 32C and 8H atoms), separated by at least 15 Å vacuum regions. The doped diamond films were constructed by substituting one C atom by a P atom in the third layer of the undoped film that corresponds to a 3 at% impurity concentration. The optimized structures are shown in Fig. 1(b). The surrounding structure of the substitution atoms is slightly strained (bond lengths are 1.61 and 1.69 Å for C–C and C–P, respectively) and the interfacial structure have a weak deformation (about 0.05 Å interfacial atomic wrinkle) because of size difference between C and substitution atom. The corresponding band structures indicate that the undoped film is a typical semiconductor with a bandgap of approximately 3 eV, whereas the P-doped film shows metallic properties, with conduction across Fermi energy. These findings are consistent with the characteristics of n-type doping semiconductor systems and with other report [39].

Based on the optimized film structures, we constructed interface sliding models by placing two diamond films against each other. The x direction, that corresponds to the $[1\bar{1}0]$ direction in the bulk diamond was selected as the sliding direction as shown in Fig. 2.

3. Results and discussion

The interaction energy $\Delta E(r)=E^{AB}(r)-E^{A}-E^{B}$, where $E^{AB}(r)$ is the total energy of the two interacting graphene layers at the interlayer distance r and $E^{A}(E^{B})$is the separate graphene energy. The energy was calculated when two sheets of graphene are brought together with a decrement of 0.05 Å. In calculating $\Delta E(r)$, the atoms in the three bottom layers of the lower slab and the three topmost layers of the upper slab have been kept fixed, while all other atoms are relaxed until the Hellmann–Feynman forces are less than 0.01 eV/Å. The calculated $\Delta E(r)$ as a function of r is shown in Fig. 3. The evident common characteristic is the increases in $\Delta E(r)$ as the distances decrease because of the increased repulsive interactions between the films for both