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Computational Chemistry Study of Diamond-like Carbon: Functions and Structure Control by Frictional Force

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1. Introduction

Diamond-like carbon (DLC) films attract the special interest of its applications as surface coatings in electronics devices, automotive engines, and so on. This is because they show excellent characteristics such as super-low friction, good wear resistance, hardness and air-tightness. In fact, DLC is used as coating on the silicon-based micro-electromechanical system (MEMS) in which friction and stiction are major problems. DLC coating maintain low friction and improve the durability and storage stability of MEMS [1]. S.A.Smallwood et al. reported that the DLC coated devices run in vacuum showed a three hundred times increase in performance over uncoated device [2]. However, in their study the atomic-scale DLC structure which shows best property remain unrevealed.

Functions of DLC films are greatly influenced by the atomic scale structure, which depends on the formation process and conditions. Also, additives in the DLC films such as H and Cr have a great influence on its function. It is therefore important to best optimize the atomic-scale structure and composition of DLC films to obtain desired functions for each application.

Computational chemistry methods are effective in nano-scale materials design and extensively applied so far [3]. In this study, we used computational chemistry methods to investigate the influence of external frictional force on the structure of DLC films. To investigate the dynamics of structure change in the complex system, a method, which can deal with chemical reaction with reasonable computational time, is necessary. Therefore, we developed a novel classical molecular dynamics program with chemical reaction extension, NEW-RYUDO-CR. We have applied the developed method to study the functions and structure of DLC controlled by frictional force.

2. Computational Method

In the developed NEW-RYUDO-CR program, it is assumed that chemical reaction could take place when interatomic distance between reacting atoms is shorter than a given distance. Probability for the reaction, P, is given as the following equation, and classical potential parameters are switched when the chemical reaction takes place during the simulation.

$$N \le P_0 \, \frac{R_{\max} - R}{R_{\max}} \tag{1}$$

 P_0 : Standard probability (constant) R_{max} : Maximum distance for chemical reaction R: Interatomic distance

CVFF potential [4] was adopted, which is generally used in organic model to express the interaction between atoms. Molecular dynamics (MD) simulation was carried out with the integration time of 0.5 fs.

3. Results and Discussion

Model Preparation

In order to prepare the structure of DLC films, we carried out the simple formation method of DLC films by NEW-RYUDO-CR. MD simulation was carried out for graphite model under extreme condition of 6000 K and 50 GPa. During the simulation, graphite structure transformed to amorphous DLC structure as shown in Fig. 1(a) (b), by the bond dissociation and formation reactions between carbon atoms. The structure was then relaxed under the ambient condition, 300 K and 1 atm. After that, we prepared Fe_2O_3 substrate above the DLC model as shown in Fig. 1(c). Then a pressure of 0.5 GPa is vertically given to the Fe₂O₃ substrate, and a shear velocity of 100 m/sec is horizontally given to the substrate to study the friction at the interface of DLC and Fe₂O₃. Hydrogenated DLC (H-DLC) model containing 20 % hydrogen was also prepared by the same method.



Fig. 1 (a) Initial graphite model (b) DLC films from graphite ($sp^2 : sp^3 = 1 : 9$) (c) frictional model



Fig. 2 Friction coefficient and structural change of H-DLC films ($sp^2 : sp^3 = 9 : 1$)

Structural change of DLC films

We studied the structure change of DLC films induced by frictional force. Fig. 2 shows the friction coefficient versus simulation time and structural changes of H-DLC films. Friction coefficient was high at the initial state, then gradually decreased, involving the structural change of H-DLC films. Dissociation reaction between carbon atoms occurred by frictional force, then the number of sp^2 carbon atoms increased. During 7 to 12 ps, friction coefficient increased, because of the transient structure change of DLC. Finally at 125 ps, the proportion of sp² and sp³ carbon bond changed to sp^2 : $sp^3 = 2$: 8. This structural change would have influences on not only the low friction property of DLC films but also other various properties. Thus, we suggest the possibility of controlling various properties of DLC films by controlling the structure of DLC films by the frictional force.

Also, structural change of DLC films with different proportions of sp² and sp³ carbons was studied. Friction coefficient of DLC films was examined as shown in Table 1. Friction coefficient increases as sp² ratio increases and takes the highest value at the proportion of sp² : sp³ = 4 : 6 then gradually becomes lower with increase of sp² carbon ratio. Friction simulation of sp² : sp³ = 4 : 6 DLC was shown in Fig. 3. In the simulation, few number of bond dissociation and formation reactions involved, then the structure of DLC films scarcely changed. To investigate the mechanism of super-low friction, the snapshots of sp² : sp³ = 9 : 1 DLC was shown in Fig. 4. As the results of friction simulation, two layers of DLC surface was broken away because of bond dissociation of carbon atoms by the fric-

 $sp^2: sp^3$ friction coefficient sp²: sp³ friction coefficient 1:9 0.058 0.051 6:4 0.032 7:3 0.050 2:80.033 3:7 0.084 8:2 0.017 4:6 0.130 9:1 5:5 0.045 Fe 0 sp² carbon sp³ carbon Initial structure 125 ps Fig. 3 Friction simulation of sp^2 : $sp^3 = 4:6$ DLC Bond dissociation E Fe 0 sp² carbon sp³ carbon Initial structure 50 ps

Fig. 4 Friction simulation of $sp^2 : sp^3 = 9 : 1$ DLC

tional force, and the upper layer adhered to Fe_2O_3 substrate. Then sliding was observed between graphite layers. By this phenomenon, DLC films which contain large proportion of sp^2 carbon atoms indicate super-low friction by sliding between graphite layers.

4. Conclusions

We have developed a novel molecular dynamics method to study the structure of DLC. The developed method was applied to the friction simulation of DLC and H-DLC films with different proportions of sp^2 and sp^3 carbon bonds. We observed the structural change of DLC, in which the number of sp^2 carbon increased with dissociation reaction by the effect of frictional force. This structural change influenced the low friction property of DLC films, and indicate the possibility of controlling various properties of DLC films by controlling the DLC structure by the frictional force.

References

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Table 1 Friction coefficient of DLC films