

First-Principles Calculation on the Structure Transition of Diamond to Graphene in Si-Doped DLC

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1. Introduction

Diamond-like carbon (DLC) coatings as solid lubricant exhibit excellent tribological properties of low friction and high wear resistance. The silicon doped DLC (DLC-Si) films were investigated by several groups, because the tribological properties of DLC could be improved by doping of silicon. They reported that the DLC-Si films showed low friction coefficient properties in a humid atmosphere. In addition, they also investigated the structure of DLC-Si films, since the sp^2 carbon (Csp^2) and sp^3 carbon (Csp^3) ratio of the DLC films significantly affect film properties. According to the visible Raman investigation of DLC-Si film [1], the graphite structure was observed in the DLC film doped by a small amount of Si atoms, while the highest Si content shows less Csp^2 in the Si-doped DLC films. The results conclude that a small amount of doping Si atoms leads to the formation of the Csp^2 graphite-like ring structure, which causes the low friction properties. However, the transition mechanism of diamond to graphite by Si atom has not been revealed in details. Thus, in the present study, we investigate the transition from Csp^3 to the Csp^2 by the first-principles calculation at atomic scale, and discuss the friction properties affected by the doped Si atoms in the DLC films.

2. Simulation method

The mechanism of the transition from Csp^3 to Csp^2 is investigated by the first-principles calculation based on the density functional theory (DFT) method. The Si-doped diamond (111) model is shown in Fig. 1 (a).

3. Results and discussions

To investigate the mechanism of the transition from Csp^3 to Csp^2 in the Si-doped diamond, we replaced one carbon atom on the top layer by a Si atom. The model of the Si-doped diamond (111) surface is optimized by the first-principles calculation. The crystal structure of Si-doped diamond is changed after the geometry optimization calculation. It is very interesting to see the formation of graphite structure as shown in Fig 1 (b). T. Iseki et al. has experimentally reported that the graphite-like ring structure was observed in the DLC-Si film, which contains a small amount of Si atoms [1]. Then, the calculation results are in good agreement with

the experimental results. The magnified picture of the structure transition from Csp^3 to Csp^2 is shown in Fig 2. Fig. 2 (a) shows the initial structure of Si-doped diamond (111) surface, and the bond lengths between carbon and Si, carbon A and B, carbon E and D take the same value of 1.698 Å. After the geometry optimization calculation, the bond length of Si-C becomes 1.88 Å since the ion radius of Si atom is larger than that of carbon. Then the carbon A and F are pushed down. The bond length between the carbon A and B decreases from 1.698 Å to 1.576 Å. After the carbon F approaches to the carbon D, the bond between carbon F and D is formed. The 6-membered ring of the Si-doped diamond (111) surface is destroyed and changes to the 5-membered ring as shown in Fig. 2 (b). Meanwhile, the carbon E moves up, and the bond length between carbon E and D increases from 1.698 Å to 2.485 Å. The bond between carbon E and D is broken, and then the Csp^3 E changes to Csp^2 . This leads that the Csp^3 G and H change to Csp^2 , indicating that the graphitic or graphene structure is formed.

The mechanism of the transition from Csp^3 to Csp^2 is investigated by the DFT method. The 6-membered rings change to 5-membered rings by Si doping and it leads to the graphene structure formation in the Si-doped diamond.

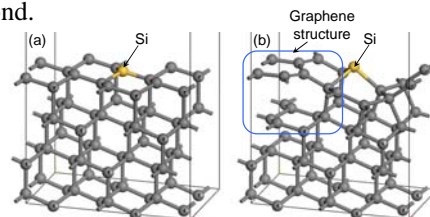


Fig. 1 The Si doped diamond (111) surfaces (a) at the initial state and (b) after optimization calculation.

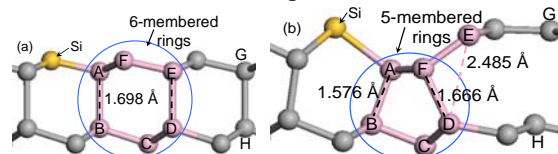


Fig. 2 The structure change of 6-membered ring to 5-membered ring. (a) The initial structure; (b) the optimized structure.

4. Reference

[1] T. Iseki et al., *Diamond Relat. Mater.* **15** (2006) 1004.