First-principles molecular dynamics studies of plasma-surface interaction

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Abstract

Experiments show that the hydrocarbon molecules CH_3 and CH_4 in fusion devices are generated mainly by chemical sputtering. We numerically examine the chemical sputtering of graphite by hydrogen atoms using the first-principles molecular dynamics simulation method based on quantum mechanics. We have shown that hydrogen atoms adsorbed on graphite break the carbon bonding of the graphite and hydrocarbon molecules are formed when they cover about a half of the graphite surface. This occurs because unstable configuration with a non-flat surface is formed due to adsorption of large number of hydrogen atoms. Moreover, we have shown that graphite is destroyed more actively in the high temperature region that models the actual fusion environment.

1. Introduction

Clarifying the interactions between plasma and wall material in the fusion devices is an important issue, and will be the basis of the new material development in the future. Roughly speaking, plasma-wall interactions consist of physical and chemical sputterings, either of which influences the other. It is estimated that the chemical sputtering can give rise to the most significant impacts on the furnace material in various phenomena [1]. On the other hand, graphite and carbon materials have been used for the plasma facing walls of many experimental nuclear fusion devices [2].

Current experimental results show that hydrocarbon molecules such as CH_3 and CH_4 are generated in the chemical sputtering. It was clarified by recent research that the pre-formation of CH_2 is necessary for the production of heavy hydrocarbon molecules CH_3 and CH_4. However, such formation processes are not yet obvious since the chemical sputtering which is a microscopic (atomic) phenomenon is not to be easily analyzed experimentally.

The attempts of numerically studying the sputtering using quantum dynamics techniques such as DFT (Density Functional Theory) [3] have been made [4,5]. It was shown that molecular orbits change from sp^2-like to sp^3-like by successive adsorption of hydrogen atoms on the carbon atom, which facilitates further adsorption of hydrogen atoms. However, there is a large energy gap between the formation of CH and CH_2 molecules [5], and the formation of CH_3 and CH_4 needs to go through this gap. Up to now, the process of CH_2

generation has not been clarified theoretically for realistic multi-layer graphite geometry. Experimentally the hydrogen absorption on graphite reaching about 40% in number of atoms leads to production of heavier hydrocarbon molecules [6,7].

In this study we adopt the system of a multi-layer graphite and hydrogen atoms, and try to examine the chemical sputtering process by means of the first-principle molecular dynamics simulation method [8].

2. Calculation method

The first-principles molecular dynamics simulation method which is derived from the Schroedinger equation of quantum mechanics was applied to various physics and chemistry fields since Car-Parrinello method was devised [8]. We solve the Kohn-Sham equation based on the density functional theory, and use the norm-conserving pseudopotential by Troullier and Martines [9]. Namely, the self-consistent electronic density is first calculated with the Kohn-Sham equation, then nuclei (atoms) are moved classically, and the whole step is repeated. For the nuclei part, either the geometry optimization is done to find an energetically favorable (minimum) geometry with the conjugate gradient (CG) method, or molecular dynamics (MD) is done for the finite temperature case using the Verlet method. In the former case, the maximum atomic displacement is limited to 0.1Å for each step to realize the stability of calculation, and the time step is 1fs for the latter. We employ the SIESTA code developed by Spanish atomic physicists [10], and use our in-house PC cluster machines of Pentium 4 with high-speed communication software [11].

Our model graphite consists of 5 layers with each layer containing 24 carbon atoms. The system is periodic in all three directions, and a large vacuum area is inserted above the set of graphite layers. The simulation unit cell is a rectangular box of $7.4 \times 8.6 \times 31.2 Å^3$ as shown in Fig.1. We pursue the evolution of a graphite-hydrogen system by adding hydrogen atoms successively between the second and third graphite layers. Even after the third layer of the graphite has saturated with hydrogen atoms, we keep on adding the hydrogen atoms. Thus, we are simulating the erosion process of the graphite that happens after the saturation state.

3. Results and discussion

3.1 Destruction mechanism of graphite

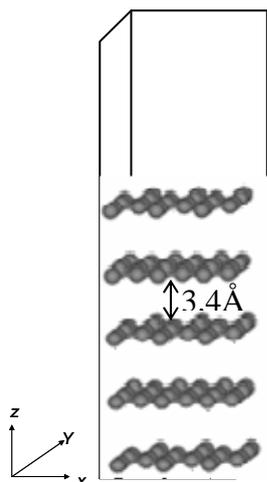Fig. 1 Simulated graphite consisting of five layers with 24x5=120 carbon atoms and a vacuum region above. The simulation box is periodic in all three directions. The distance between the layers is 3.4 Å.
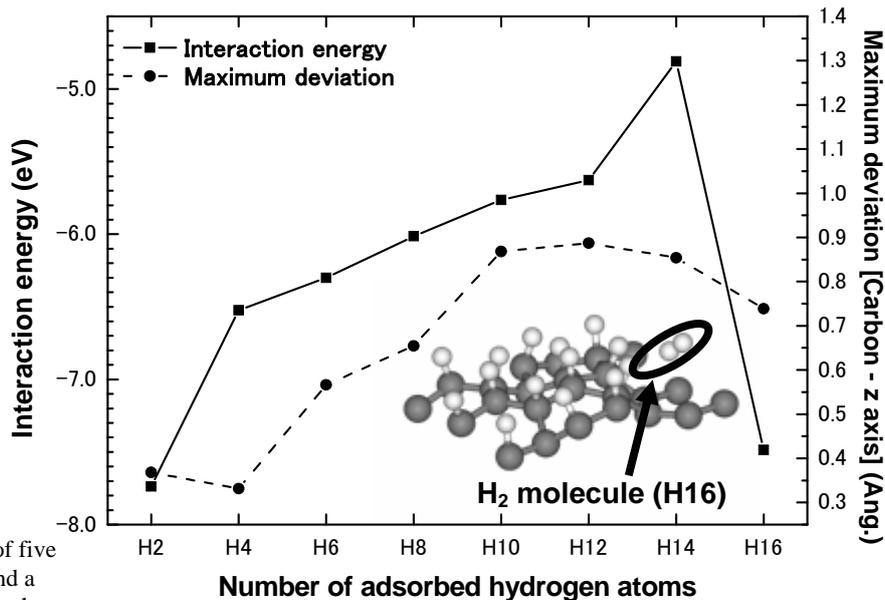

Fig. 2 Dependence of interaction energy and maximum deviation of carbon atoms along the z-axis on the number of added hydrogen atoms. The molecular picture is the third graphite layer after structural optimization when 16 hydrogen atoms are added. White and gray balls denote hydrogen and carbon atoms, respectively.

Here we describe the hydrogen adsorption to graphite and destruction (etching) of its surface, obtained by our first-principles molecular dynamics simulations. The results shown in Figs.2-5 are calculated with the geometry optimization method mentioned above.

Figure 2 shows the measured interaction energy and maximum deviation of carbon atoms in the z-direction versus the number of hydrogen atoms; they are added by two atoms at a time between the second and third layers of the graphite. The interaction energy E_{int} is calculated according to the following formula:

$$E_{int} = E_{aft} - (E_{bef} + nE_H),   (1)$$

where E_{bef} and E_{aft} are the electronic energy of the entire system before and after addition of n hydrogen atoms, respectively, and nE_H is n times the electronic energy of one hydrogen atom. The maximum deviation of the carbon atoms perpendicular to the surface is measured for those that belong to the third layer, where the deviation is the displacement from the non-perturbed level of the third layer. The figure shows that the interaction energy peaks when the number of added hydrogen atoms is about 14 (24 carbon atoms/layer), and that the interaction energy goes down after that. We find that the interaction energy increases as hydrogen atoms are adsorbed and the carbon atoms are lifted above the graphite surface. It is considered that the lifting of carbon atoms by the hydrogen adsorption makes destruction of graphite easy. We see that when two hydrogen atoms are newly added to the graphite that has already adsorbed 14 hydrogen atoms in Fig.2, a hydrogen molecule H_2 is formed instead of being adsorbed on bare carbon as it should be energetically

more favorable. On the other hand, another simulation generated CH_2 steadily where four hydrogen atoms are newly added to the graphite that has already adsorbed 12 hydrogen atoms. Therefore, the graphite saturated with about one-half the adsorbed hydrogen atoms in number compared to carbon atoms, leads to the formation of CH_2 by high probability which results in destruction of graphite.

The result of adding only one hydrogen atom between two layers when the third layer has already adsorbed ten hydrogen atoms is shown in Fig. 3. The possibility of destroying graphite was checked by a previous work [5], which showed that the carbon atom that forms CH_2 needs to be lifted from the planar graphite surface so that the distances between such carbon atoms become larger than the equilibrium bond length. In the leftward molecular picture of Fig.3 where [H]/[C] ~ 0.46, CH_2 is once formed but it is not lifted completely which is energetically not isolated from surrounding CH. Thus, this CH_2 is reunited with an adjacent carbon atom by releasing the hydrogen, and the graphite is recovered. Destruction of graphite by under-saturated state with hydrogen atoms is not possible.

The result of the run when five hydrogen atoms are added at the same time is shown in Fig.4. We see perfect destruction of graphite and the stable formation of CH_2 – some 6-membered carbon rings are broken and carbon atoms are not aligned in a plane. A big hole is created at the destroyed site where [H]/[C] ~0.75 (Fig.5). Through this hole, hydrogen atoms can easily penetrate to the lower layer, destroy the graphite layer there, and the destruction can proceed deeply inside the graphite.
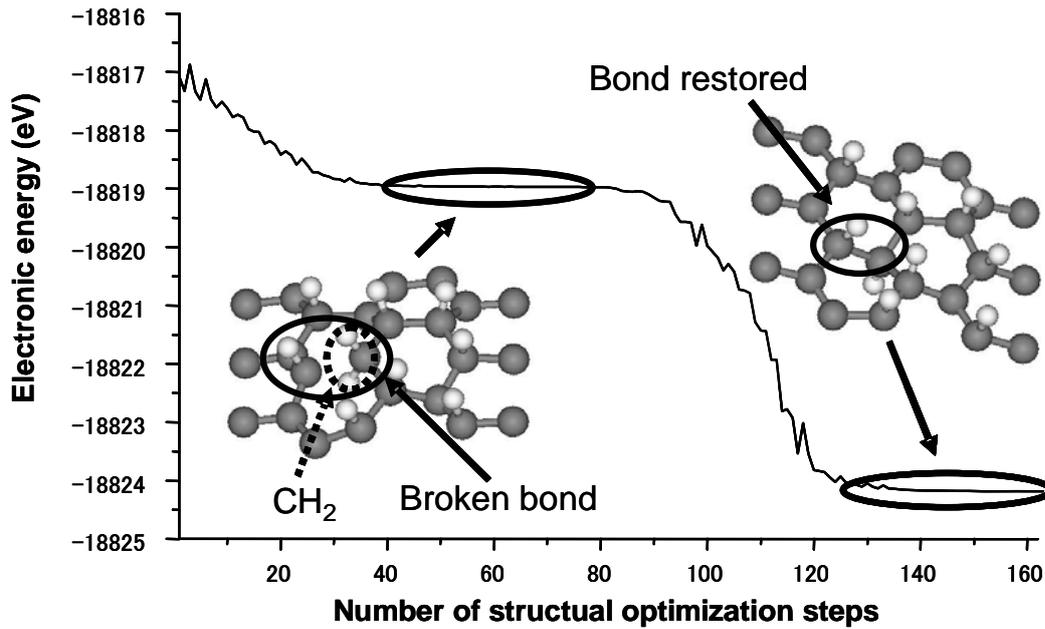
Fig. 3 Change of the electronic energy against the number of geometry optimization steps is shown for the case when one hydrogen atom is added to graphite which has adsorbed ten hydrogen atoms. The molecular pictures show two quasi-steady configurations. White and gray balls denote hydrogen and carbon atoms, respectively.
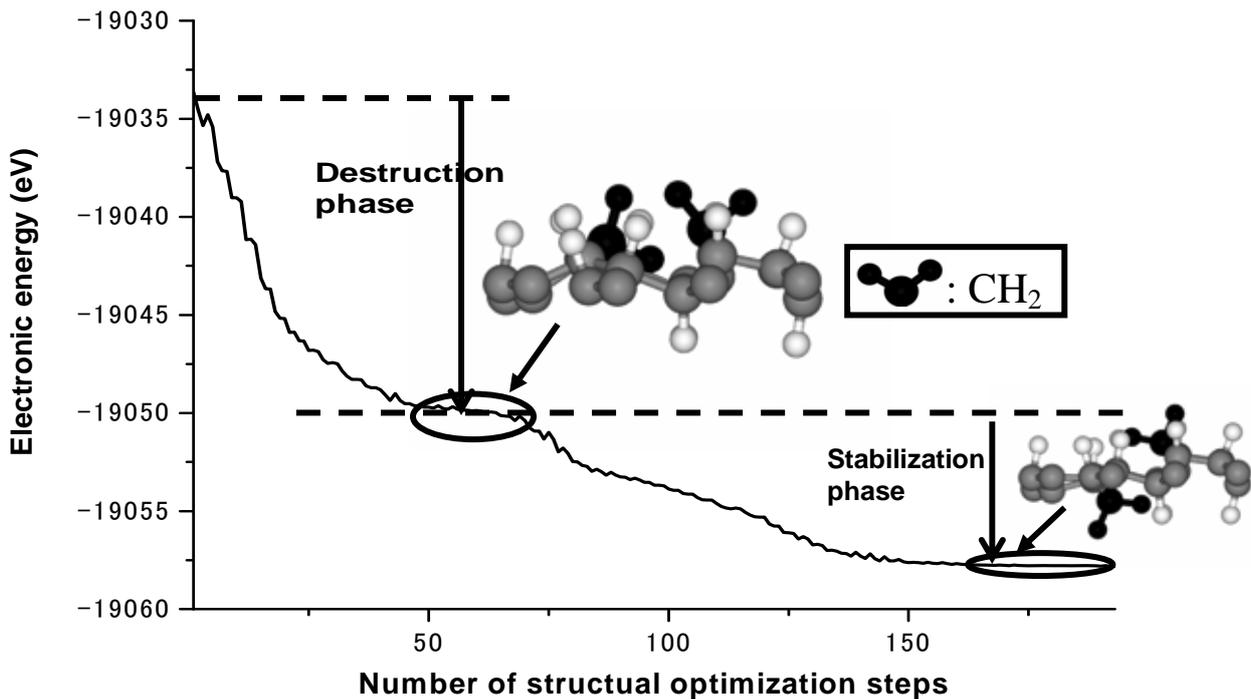

Fig. 4 Electronic energy is shown for the case when five hydrogen atoms are added simultaneously. The molecular pictures are those of the third layer at quasi-steady states. White and gray balls denote hydrogen and carbon atoms, respectively, and a black molecule denotes CH_2.

The above phenomena may be generated by the following mechanism. A carbon atom has four valence electrons in the outermost shell. The carbon atom in graphite has three neighbors, thus it can easily receive one hydrogen atom to form stable C-CHC-C. However, to accept one more hydrogen atom, at least one of the

C-C bonds must be cut to form C-CH$_2$-C which must go over a large energy barrier for normal graphite [5]. On the other hand, when many hydrogen atoms have already been adsorbed to graphite, such graphite is no longer a planar configuration but some CHs are lifted
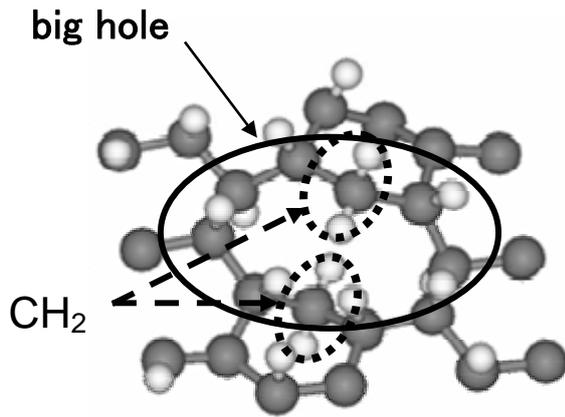
Fig. 5 Destroyed graphite and emergence of a big hole for the final step of Fig.4. White and gray balls denote hydrogen and carbon atoms, respectively, respectively.
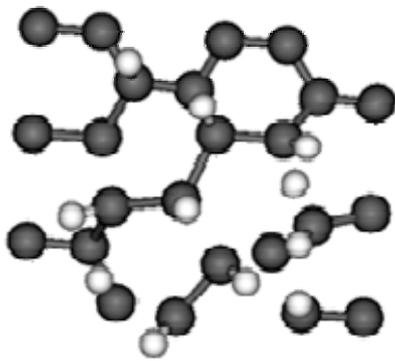

Fig. 6 Appearance of destroyed graphite at 900K. White and gray balls denote hydrogen and carbon atoms, respectively.

up or down from the initial plane. The 6-membered carbon rings are distorted, and bond lengths between carbon atoms are larger than the normal C-C distance. That is, such CHs can accept a new hydrogen atom and break the C-C bond with little energy penalty to form C-CH_2-C. This mechanism is consistent with the observations in our simulation.

3.2 Graphite destruction at high temperature

Next, the graphite destruction process is examined under a high temperature in-furnace environment. According to experimental results, the plasma with the temperature 1000K comes in contact with the wall in the fusion devices. The amount of methane generation by erosion becomes most active in these temperature range [12]. We expect that the chemical sputtering actively occurs there. Figure 6 shows the simulation result for the graphite of 900K by Verlet molecular dynamics with the Nose-thermostat. It is confirmed, as shown in Fig.6, that the destruction occurs more actively than for the 0K (cold) case simulated with the CG method. We insist that this effect is important to

understand the chemical sputtering under actual fusion device environments.

4. Conclusion

In this work we studied the destruction of graphite by means of the first-principles (quantum mechanical) molecular dynamics simulation method. We showed that a disturbed graphite state with a non-planar surface appears when the hydrogen adsorption on the graphite reaches the saturated condition, [hydrogen atoms]/ [carbon atoms] ~ 40-50%, and that the destruction of graphite follows. Moreover, we found that the steadily formed CH_2 are lifted above the graphite surface in the destruction process, but that the detachment of a hydrocarbon molecule is difficult if the number of hydrogen atoms attached on one carbon atom is two or less. It was also shown that the destruction of graphite occurs more actively in the high temperature case. On the other hand, it remains to be clarified by what kind of mechanism the destruction proceeds in the high temperature region.

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