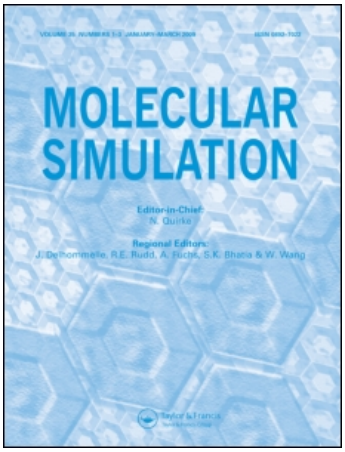

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular dynamics simulation of sputtering process of hydrogen and graphene sheets

H. Nakamura[a]; A. Ito[b]
[a] National Institute for Fusion Science, Gifu, Japan [b] Department of Physics, Graduate School of Science, Nagoya University, Nagoya, Japan

To cite this Article Nakamura, H. and Ito, A.(2007) 'Molecular dynamics simulation of sputtering process of hydrogen and graphene sheets', Molecular Simulation, 33: 1, 121 — 126
To link to this Article: DOI: 10.1080/08927020601078471
URL: http://dx.doi.org/10.1080/08927020601078471

Molecular Simulation, Vol. 33, Nos. 1–2, 15 January–15 February 2007, 121–126

Molecular dynamics simulation of sputtering process of hydrogen and graphene sheets

H. NAKAMURA†* and A. ITO‡

†National Institute for Fusion Science, Oroshi-cho, Toki, Gifu 509-5292, Japan
‡Department of Physics, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

(Received July 2006; in final form October 2006)

To clarify the yielding mechanism of small hydrocarbon molecules in chemical sputtering between hydrogen and graphene sheets, we made a classical molecular dynamics simulation with modified Brenner's REBO potential, which we proposed to deal with chemical reaction. As the simulation model, we prepared a more realistic physical system, which is composed of 160 incident hydrogen atoms and ten graphene multilayers, than our previous model. From the present work, we found the following fact: breaking the covalent bonds between carbon atoms by hydrogen does not play an important role during the destruction process of graphene structure, but momentum transfer from incident hydrogen to graphene causes it to destroy graphene structure. Moreover, it is found that almost all fragments of graphene sheets form chain-shaped molecules, and that yielded hydrocarbon molecules are composed of carbon chain and single hydrogen-atom.

Keywords: Graphene; Graphite; Hydrocarbon; Sputtering; Molecular dynamics; Brenner potential

1. Introduction

Plasma–carbon interaction yields small hydrocarbon molecules on the divertor region of a nuclear fusion device [1]. Diffusing from divertor region to core plasma region of fusion device, generated hydrocarbon takes energy from the core plasma. Therefore, the hydrocarbon is sometimes called "dust" by the nuclear plasma researchers. It was reported that the chemical sputtering yields of CH_4 and C_2H_l (l is a positive integer) have been measured at divertor plates of plasma equipment [1]. According to Nakano *et al.*, the CH_4 yield is less than 0.8% and the C_2H_l yield is 1–2% at the surface temperature of 380 K. However, the creation mechanism of the hydrocarbons has not been elucidated yet.

As the first step to clarify the creation mechanism, we investigated, by computer simulation, the collision process of hydrogen atoms and one graphene sheet, which is regarded as one of the basic processes of complex plasma–carbon interaction in the previous work [2]. In the previous simulation, we used a "classical" molecular dynamics (CMD) algorithm with the modified Brenner's REBO potential which we proposed to deal with the chemical reaction between hydrogen and graphene [2,3]. From the previous work [2] in which an incident hydrogen kinetic energy E_I is less than 100 eV to compare with experiments of divertor, it was found that an hydrogen-absorption rate of one graphene sheet depends on the incident hydrogen energy, and that the collision mechanism between a graphene and a hydrogen can be classified into three types of processes: absorption process for $E_I < 5$ eV, reflection process for $5\,\text{eV} < E_I < 50\,\text{eV}$, and penetration process for $E_I > 50$ eV. Moreover, it was also found that when hydrogen atom is absorbed by graphene, the nearest carbon atom overhangs from the graphene, which we called "overhang structure".

Based on the above results, simulation model are extended from a single graphene sheet to multilayer graphene sheets in the present work. We adopt three cases (5, 15 and 100 eV) as the incident energies of the hydrogen atoms E_I. Each value corresponds to the absorption, the reflection and the penetration process of the collision between single graphene sheet and hydrogen atoms, respectively. Moreover, we use the same simulation algorithm and the same interaction potential as the previous single-graphene sheet simulation [2]. The aim of

*Corresponding author. Email: nakamura@tcsc.nifs.ac.jp

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020601078471

the extension of simulation model is that we reveal a more realistic sputtering process of graphene sheets and hydrogen atoms than the previous work.

In Section 2, we review the simulation method including the interaction potential, which was proposed in the previous work. We discuss the simulation results and compare them with the experiment in Section 3 and summarize a conclusion in the last Section 4.

2. Simulation method

The simulation algorithm and the interaction potential are almost the same as the previous work [2]. First, we review the interaction potential among hydrogen and graphite atoms. The original Brenner's REBO potential [3], which was proposed on the basis of past simulations [4–6], has the following form:

$$U = \sum_{i,j(>i)} [V^{\mathrm{R}}(r_{ij}) - \bar{b}_{ij}(\{\mathbf{r}\})V^{\mathrm{A}}(r_{ij})], \tag{2.1}$$

where r_{ij} is the distance between atoms i and j, V^{A} is an attractive term, V^{R} is a repulsive term and the function $\bar{b}_{ij}(\{\mathbf{r}\})$ includes all effects of molecular orbitals. However, if chemical reaction occurs, the REBO potential breaks energy conservation. Therefore, we proposed the following new function N_{ki}^{t} expressing conjugation effects [2]:

$$N_{ij}^{\mathrm{conj}} \equiv 1 + \sum_{k(\neq i,j)}^{\mathrm{carbon}} f^{\mathrm{c}}(r_{ik}) Q\left(N_{ki}^{\mathrm{t}}\right) + \sum_{l(\neq j,i)}^{\mathrm{carbon}} f^{\mathrm{c}}(r_{jl}) Q\left(N_{lj}^{\mathrm{t}}\right). \tag{2.2}$$

The cut-off function f^{c} is defined by the following form [3]:

$$f^{\mathrm{c}}(x) \equiv \begin{cases} 1 & \text{if } x \leq D_{\min}, \\ \frac{1}{2}\left[1 + \cos\left\{\pi \frac{x - D_{\min}}{D_{\max} - D_{\min}}\right\}\right] & \text{if } D_{\min} < x \leq D_{\max}, \\ 0 & \text{if } x > D_{\max} \end{cases} \tag{2.3}$$

where the values of $D_{\min}$ and $D_{\max}$ are given in table 1. If the distances among particles are smaller than $D_{\min}$, the particles are regarded as connecting with covalent bonds. As the distance between two particles is becoming larger than $D_{\min}$ and reaches $D_{\max}$, the function f^{c} goes from one to zero.

Table 1. Values of $D_{\min}$ and $D_{\max}$ for pairs of atoms [3].

	D_{min} (Å)	D_{max} (Å)
C—C	1.7	2.0
C—H	1.3	1.8
H—H	1.1	1.7

The function Q and the parameter N_{ki}^{t} in equation (2.2) are defined as follows:

$$Q(x) \equiv \begin{cases} 1 & \text{if } x \leq 2, \\ \frac{1+\cos\{\pi(x-2)\}}{2} & \text{if } 2 < x \leq 3, \\ 0 & \text{if } x > 3, \end{cases} \tag{2.4}$$

$$N_{ki}^{\mathrm{t}} \equiv \sum_{j(\neq k,i)} f^{\mathrm{c}}(r_{kj}). \tag{2.5}$$

Modified Brenner's REBO potential, which is given by the above equations, conserves the total energy during the chemical reaction.

Next, we explain the simulation model in the present work. We prepare ten graphene layers each of which is composed of 160 carbon atoms. All the layers are perpendicular to the z-axis and have periodic boundary conditions for x and y directions. Distance between graphene sheets was set to 3.348 Å in the initial state. Graphite atoms at four corners of the first graphene sheet from the top are fixed in all simulations. These four corners belong to the same plane, which forms the $z = 0$ plane. We define the original point of coordinates as the center of gravity of the four corner atoms.

In the second graphene sheet, the center graphene atom is fixed at $(x, y, z) = (0, 0, -3.348\,\text{Å})$. After the third graphene sheet and later, the above fixed condition is repeated in all layers. As the initial condition of the graphene layers, we prepare the equilibrium state of carbon atoms in all graphenes with a temperature 300 K.

We shot one incident hydrogen atom at a time every 5×10^{-14} seconds from $z = 120$ Å plane to the first graphene which is located at $z = 3.348\,\text{Å} \times (4 + 1/2) = 15.066$ Å, until the total number of the hydrogen atoms becomes 160. We make the three simulations each incident hydrogen of which is set to 5, 15 or 100 eV, respectively. The $x - y$ coordinates of the incident hydrogen atom at $z = 120$ Å plane are given as a pair of random numbers ever time. Each injection angle of the incident hydrogen atom between z-axis is set to a uniform random number from 0 to 60°.

If an incident hydrogen atom is reflected by the graphenes and reaches $z = 120$ Å plane, the reflected hydrogen atom is omitted from the simulation. If the incident atom penetrates the graphene sheets and reaches $z = -120$ Å plane, the penetrated hydrogen atom is also omitted from the simulation.

To integrate the equation of the motion, the second-order symplectic integration method is used in our simulation [7–10].

3. Simulation results and discussions

We simulated sputtering process of hydrogen atoms and graphene sheets with the three incident-energy cases, namely $E_{\mathrm{I}} = 5$ eV, $E_{\mathrm{I}} = 15$ eV and $E_{\mathrm{I}} = 100$ eV. Each incident energy corresponds to absorption process,

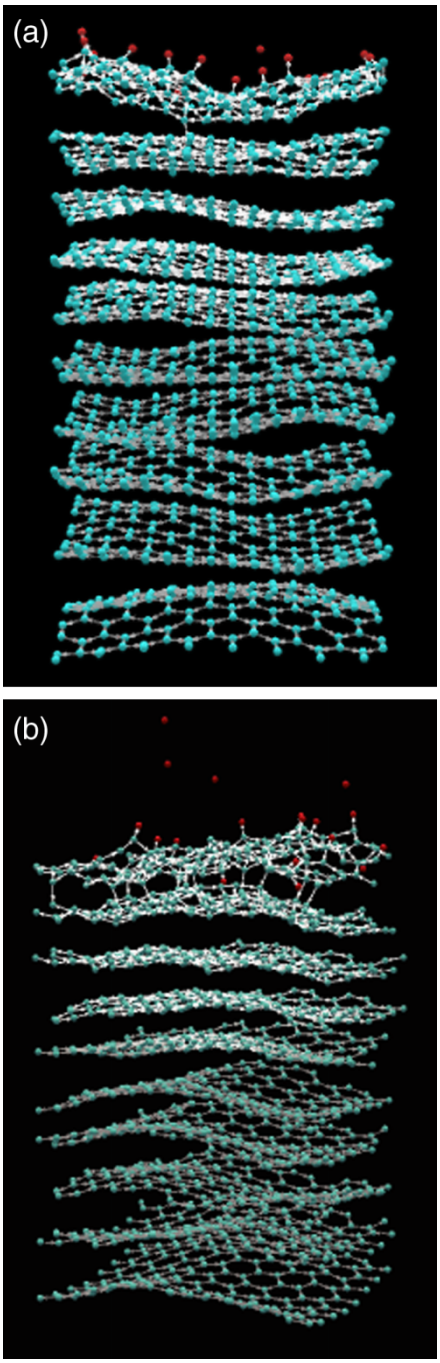

Figure 1. Snapshots of graphene multilayer structure and injected hydrogen atoms in the case that $E_I = 5$ eV. Henceforth, the red and blue balls represent the hydrogen and carbon atoms, respectively: (a) about 15 hydrogen atoms connect with the graphene sheet in the case that the total number of the injected hydrogen atoms n_H is 79. Each hydrogen atom and the surrounding carbon atoms compose the stable "overhanged" state; (b) n_H has increased to 159 and the first graphene sheet contacts with the second one. The graphene structure is damaged. The increase in the number of the overhanged hydrogen atoms is not as large as the increase in n_h, i.e. $159 - 79 = 80$. The third sheet remains almost unchanged (colour in online version).

reflection process or penetration process of sputtering between a single graphene sheet and a hydrogen atom, respectively [2]. We show snapshots of graphene multilayer structure and injected hydrogen atoms in the above

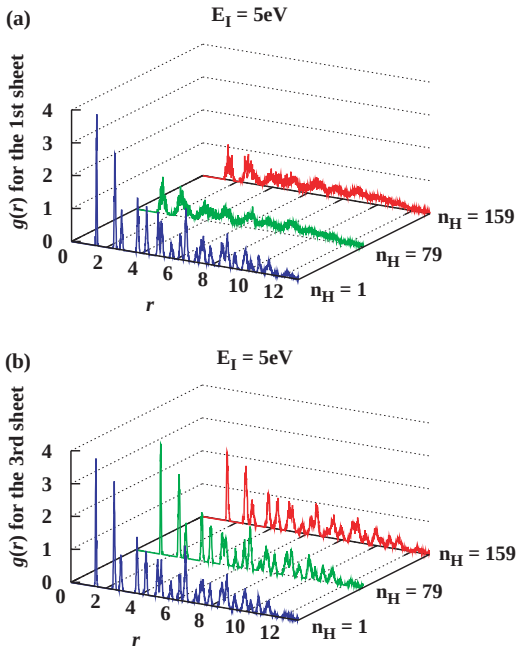

Figure 2. Radial distribution functions $g(r)$ among carbon atoms in the first (a) and the third (b) graphene sheets for the three cases $n_H = 1$ (blue), $n_H = 79$ (green) and $n_H = 159$ (red), where n_H denotes the total number of injected hydrogen atoms. The incident hydrogen energy is 5 eV (colour in online version).

three cases in figures 1, 3 and 5, respectively. We also plot the radial distribution functions of carbon atoms for the first and the third sheets from the top in figures 2, 4 and 6. Detail of each simulation result is shown in the followings subsection.

3.1 *The case of* $E_I = 5$ eV

This situation corresponds to the absorption process between a hydrogen atom and a single graphene sheet [2]. It was intuitively expected that incident hydrogen atoms destroy the graphene multilayer structure from the surface graphene sheet by breaking covalent bonds between carbon atoms. The present simulation results show that our prediction is partially correct and that the surface graphene, which is exposed to hydrogen atoms, is broken first. Contrary to our prediction, however, the leading cause of destruction of graphene sheet is not that the incident hydrogen breaks the covalent bond between carbon atoms, but that the incident hydrogen transfers its momentum to the carbon in the first graphene sheet (figure 1(a)). The first graphene sheet, which gained momentum from the incident hydrogen, undulates more deeply, as hydrogen atoms are injected. In course of time, amplitude of undulation becomes the same large as the distance of layers and the first graphene sheet contacts with the second one; then, the carbon in the first sheet interacts with the carbon in the second sheet (figure 1(b)). Thus, the first and the second sheets deform and their honeycomb-structures are broken. The simulation in the next case of $E_I = 15$ eV makes it clear that breaking

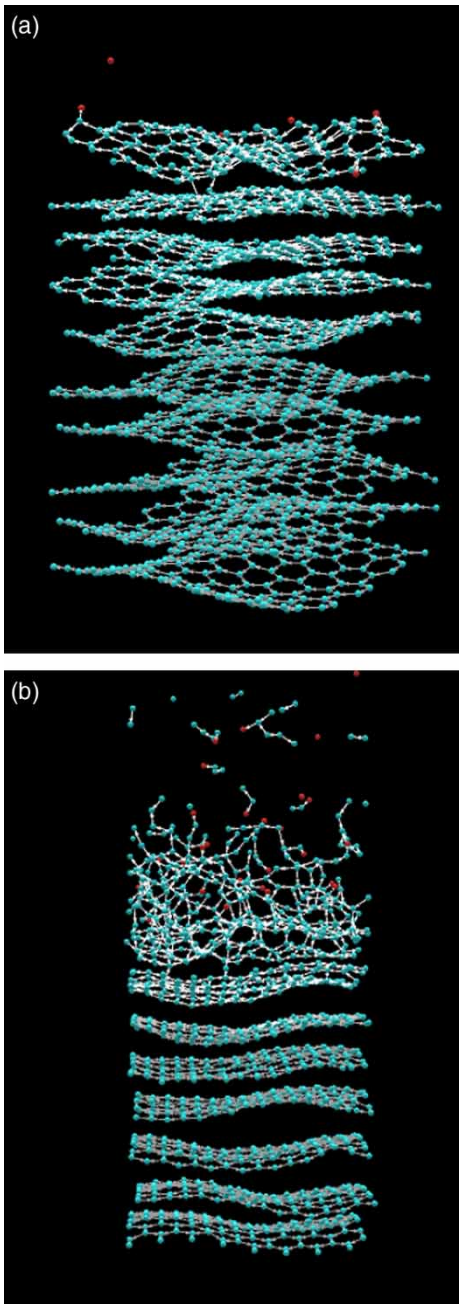

Figure 3. Snapshots of graphene multilayer structure and injected hydrogen atoms in the case that $E_I = 15$ eV: (a) four hydrogen atoms connect with the graphene sheet in the case that the total number of the injected hydrogen atoms n_H is 30. Each hydrogen atom and the surrounding carbon atoms compose the stable "overhanged" state; (b) n_H has increased to 159 and the first graphene sheet contacts with the second one. Thus, the graphene structure is damaged. Fragments of graphene sheets and hydrogen atoms form chain-shaped molecules. The third sheet remains almost unchanged.

covalent bonds between carbon by hydrogen do not play an important role in the above destruction mechanism.

In figure 2(a), we plot the radial distribution functions $g(r)$ among carbon atoms in the first graphene sheet for the three cases $n_H = 1$, $n_H = 79$ and $n_H = 159$, where n_H denotes the total number of injected hydrogen atoms. This figure shows that, as injected hydrogen atoms increases,

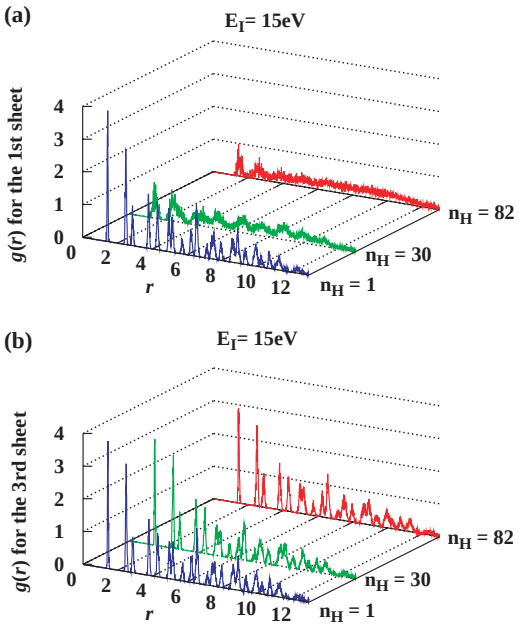

Figure 4. The radial distribution functions $g(r)$ among carbon atoms in the first (a) and the third (b) graphene sheets for the three cases $n_H = 1$ (blue), $n_H = 30$ (green) and $n_H = 82$ (red). The incident hydrogen energy is 15 eV (colour in online version).

the graphene structure of the first graphene sheet is breaking. On the other hand, figure 2(b) shows that $g(r)$ among carbon atoms in the third graphene sheet remains almost unchanged during hydrogen injection, which denotes that the third sheet is not destroyed by hydrogen.

3.2 *The case of* $E_I = 15$ eV

The second situation corresponds to the reflection process of a hydrogen atom from a single graphene sheet [2]. Therefore, it is expected that it is difficult for hydrogen to connect with graphene sheet. This prediction is confirmed by figure 3(a), which shows that the number of overhanged hydrogen atoms is only four in spite of the fact that $n_H = 30$. From this figure and figure 4(a), deformation of the first graphene sheet is recognized in the case that $n_H = 30$. By the above fact and the simulation result in the case that $E_I = 5$ eV, we reached the following conclusion: breaking the covalent bonds between carbon atoms by hydrogen does not play an important role during destruction process of graphene structure, but momentum transfer from incident hydrogen to graphene causes to break graphene structure.

Furthermore, we obtained new information about structures of hydrocarbon and carbon molecules, which are yielded by sputtering. From figure 3(b), it is found that almost all fragments of graphene sheets form chain-shaped molecules, and that yielded hydrocarbon molecules are composed of carbon chain and single hydrogen-atom.

We obtain the yield ratio $Y_{C_lH_m}$ of hydrocarbon molecule C_lH_m (l is a positive integer, and m is a non-

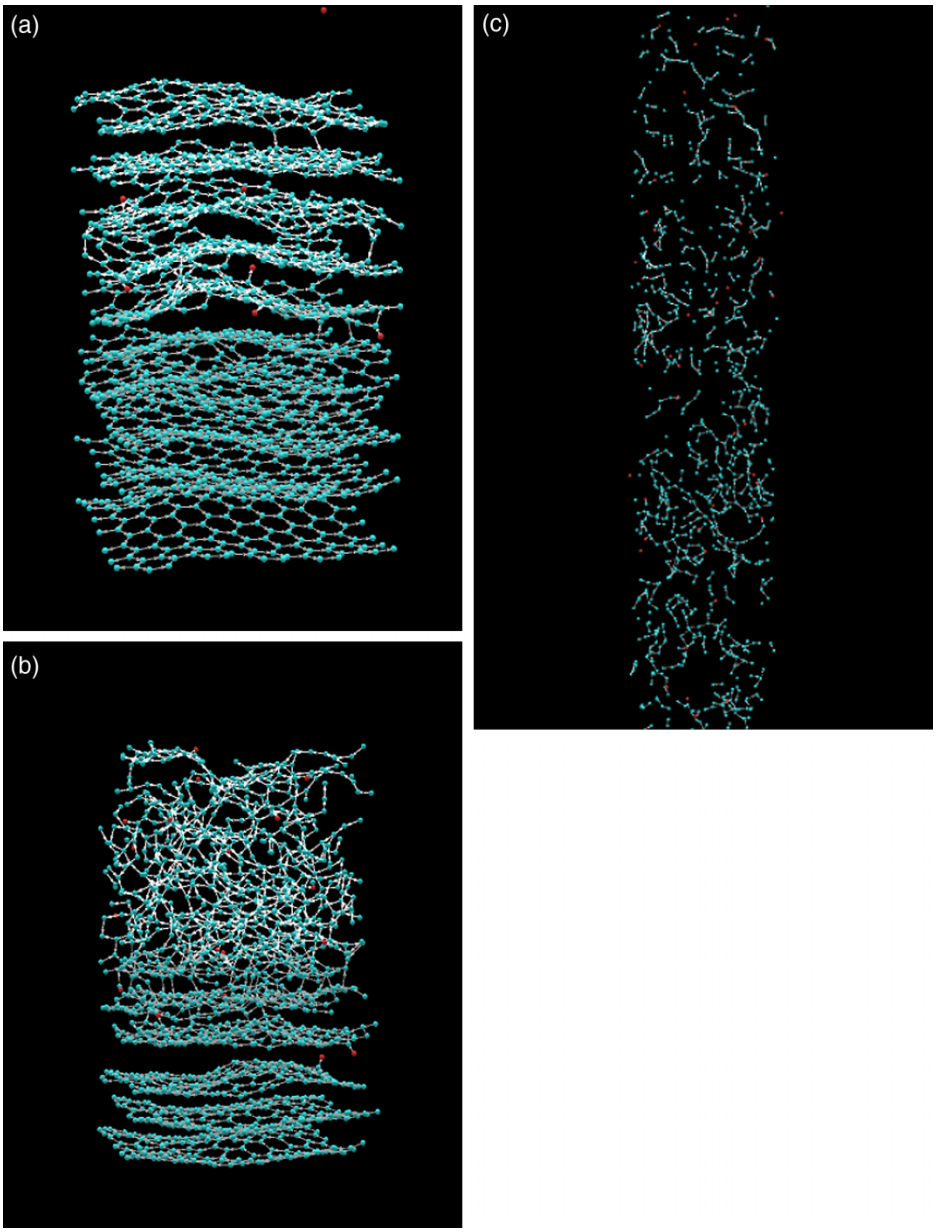

Figure 5. Snapshots of graphene multilayer structure and injected hydrogen atoms in the case that $E_I = 100$ eV: (a) after injecting hydrogen atoms penetrate several graphene sheets, hydrogen atoms contact with the graphene sheet in the case that the total number of the injected hydrogen atoms n_H is 8. Graphene sheet is connected in both sides with hydrogen; (b) n_H has increased to 30 and the upper five graphene sheets contact with other sheets; (c) graphene structure has already been broken to chain molecules when n_h becomes 159.

negative integer), which is defined by the ratio of the number of hydrocarbon molecules $n_{C_lH_m}$ to n_H. By counting the number of hydrocarbons, it was found that $n_C = 9$, $n_{CH} = 6$, $n_{C_2} = 12$ and $n_{C_2H} = 3$. Therefore, we have that $Y_{CH} = 6/160 \sim 3.7\%$ and $Y_{C_2H_l} = (12 + 3)/160 \sim 9\%$. From Nakano *et al.*, it was reported that $Y^{ext}_{CH_4} \sim 0.8\%$ and $Y^{ext}_{C_2H_l} \sim 1$–2%. Comparing the above values, we found that the simulation results are larger than the experiment ones. The reason of the difference might be that the interval between hydrogen injections in our simulation is million times as short as that of the experiment to make simulation time less than 2 days. To close the gap between the simulation and the experiment, the simulation time must be longer than the present one. However, it is unrealistic to extend the simulation time to million days. To overcome the above problem, for example, it is consider to simplify the simulation model by the coarse-grained method.

3.3 The case of $E_I = 100$ eV

The last situation corresponds to the penetration process of a hydrogen atom from a single graphene sheet [2]. Injected hydrogen penetrates several graphene sheets with losing their kinetic energy, which is transferred to graphene sheets, until their energy becomes of the order of a few 10 eV. After that, the hydrogen atoms begin to connect with carbon atoms (figure 5(a)). From the standpoint of

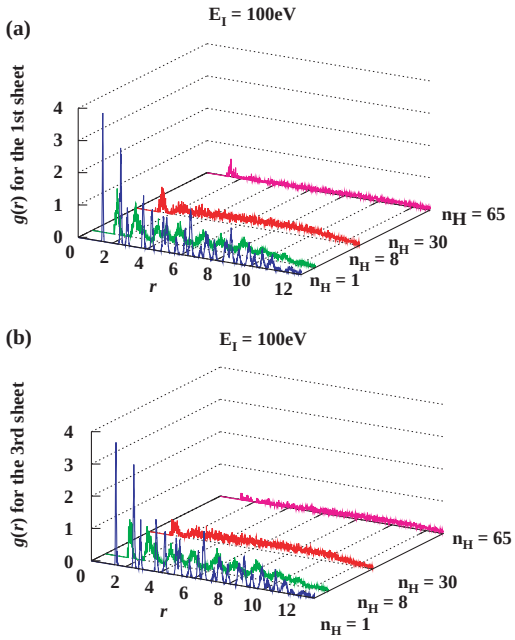

Figure 6. Radial distribution functions $g(r)$ among carbon atoms in the first (a) and the third (b) graphene sheets for the four cases $n_{\mathrm{H}} = 1$ (blue), $n_{\mathrm{H}} = 8$ (green), $n_{\mathrm{H}} = 30$ (red) and $n_{\mathrm{H}} = 65$ (pink). The incident hydrogen energy is 100 eV. The function $g(r)$ of the third sheet is similar to that of the first sheet (colour in online version).

graphene sheets instead of hydrogen, only one side of graphene sheet is exposed to hydrogen injection in the cases that $E_{\mathrm{I}} = 5$ eV and $E_{\mathrm{I}} = 15$ eV. However, in the case of $E_{\mathrm{I}} = 100$ eV, both sides of graphene sheets are attacked by hydrogen atoms. Therefore, graphene structure is destroyed rapidly in a wide range (figure 5(b),(c)). Figure 6 shows that the third sheet is destroyed in the almost same timing as the first sheet.

At the last stage of the simulation, all carbon molecules form chain-shaped structure.

4. Conclusion

The destruction process of graphene multilayer due to hydrogen injection is demonstrated by CMD with the modified REBO potential. From our simulation, we clarify the destruction process of graphene sheets as follows: (1) hydrogen atoms transfer their momentum to graphene sheet; (2) the graphene is undulated and touches the neighboring graphene sheets; (3) inter-sheet interaction of carbon atoms works and breaks graphene structure. Moreover, it is found that almost all fragments of graphene sheets form chain-shaped molecules, and that yielded hydrocarbon molecules are composed of carbon chain and single hydrogen-atom.

Acknowledgements

The work is supported partly by the National Institutes of Natural Sciences undertaking for Forming Bases for Interdisciplinary and International Research through Cooperation Across Fields of Study, and partly by Grand-in Aid for Exploratory Research (C), 2006, No. 17540384 from the Ministry of Education, Culture, Sports, Science and Technology.

References

[1] T. Nakano, H. Kudo, S. Higashijima, N. Asakura, H. Takenaga, T. Sugie, K. Itami. Measurement of the chemical sputtering yields of CH_4/CD_4 and C_2H_x/C_2D_x at the carbon divertor plates of JT-60U. *Nucl. Fusion*, **42**, 689 (2002).
[2] A. Ito, H. Nakamura. Molecular dynamics simulation of collision between graphite and hydrogen atom. *J. Plasma Phys.*, in press. Available on line at: arXiv.org:cond-mat/0604543.
[3] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott. A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. *J. Phys. Condens. Matter*, **14**, 783 (2002).
[4] P.M. Morse. Diatomic molecules according to the wave mechanics. II. Vibrational levels. *Phys. Rev.*, **34**, 57 (1929).
[5] G.C. Abell. Empirical chemical pseudopotential theory of molecular and metallic bonding. *Phys. Rev. B*, **31**, 6184 (1985).
[6] J. Tersoff. New empirical approach for the structure and energy of covalent systems. *Phys. Rev. B*, **37**, 6991 (1988).
[7] M. Suzuki. Fractal decomposition of exponential operators with applications to many-body theories and Monte Carlo simulations. *Phys. Lett. A*, **146**, 319 (1990).
[8] K. Umeno, M. Suzuki. Symplectic and intermittent behaviour of Hamiltonian flow. *Phys. Lett. A*, **181**, 387 (1993).
[9] N. Hatano, M. Suzuki. Finding exponential product formulas of higher orders. In *Quantum Annealing and Related Optimization Methods*, A. Das, B.K. Chakrabarti (Eds.), Lecture Notes Phys. Vol. 679, Springer, Heidelberg. Available on line at: arXiv.org: math-ph/0506007 (2005).
[10] H. Yoshida. Construction of higher order symplectic integrators. *Phys. Lett. A*, **150**, 262 (1990).