Molecular Dynamics Simulation of Chemical Sputtering of Hydrogen Atom on Layer Structured Graphite

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Abstract. Chemical sputtering of hydrogen atom on graphite was simulated using molecular dynamics. Especially, the layer structure of the graphite was maintained by interlayer intermolecular interaction. Three kinds of graphite surfaces, flat (0 0 0 1) surface, armchair (1 1 $\bar{2}$ 0) surface and zigzag (1 0 $\bar{1}$ 0) surface, are dealt with as targets of hydrogen atom bombardment. In the case of the flat surface, graphene layers were peeled off one by one and yielded molecules had chain structures. On the other hand, C_2H_2 and H_2 are dominant yielded molecules on the armchair and zigzag surfaces, respectively. In addition, the interaction of a single hydrogen isotope on a single graphene is investigated. Adsorption, reflection and penetration rates are obtained as functions of incident energy and explain hydrogen retention on layered graphite.

1. Introduction

In the research into nuclear fusion, we deal with plasma wall/surface interaction (PWI/PSI). In the experiment of plasma confinement, a portion of hydrogen plasma flows into divertor walls, which are shielded by the tiles of polycrystalline graphite or carbon fiber composite. The hydrogen plasma with weak energy erodes these graphite tiles and then hydrocarbon molecules such as CH_x and C_2H_x are generated. This process is called chemical sputtering. The hydrocarbon molecules affect the plasma confinement. The PSI/PWI has been researched by both of experiments [1, 2] and theory. Especially, to clarify the dynamics of atoms and molecules, molecular dynamics (MD) simulation is used [3-5].

In the present work, hydrogen atom bombardment on graphite is investigated by use of the MD simulation. Above all, the graphite which has layered structure is treated. The layered graphite has three kinds of surfaces which are flat (0 0 0 1), armchair (1 1 $\bar{2}$ 0) and zigzag (1 0 $\bar{1}$ 0) surfaces. It is simply expected that these three kinds of surfaces cause difference in the chemical sputtering and hydrogen dynamics in graphite related to the hydrogen retention.

The ITER will use tritium. However, we cannot easily experiment the PSI/PWI using tritium because of radiation risk and production cost. Therefore, advanced research for tritium by simulation is important. When we tried to investigate tritium effects in the chemical sputtering on the graphite, the tritium effects hardly appear. We consider that the cause is that the incident flax of the MD simulation is higher than that of experiments. However, in the case of a single hydrogen isotope on a single graphene, the difference of adsorption, reflection and penetration rates between hydrogen isotopes were found [6]. We extend the study of the interaction between a hydrogen isotope and a graphene in this paper. Moreover, in the viewpoint of the dumping of divertor tiles and the recycling of tritium, retention should be investigated. We demonstrate that the hydrogen retention in the layered graphite is understood by using the result of the MD simulation of a hydrogen atom and a graphene.

2. Simulation Method

2.1. System of Three Kinds of Layered Graphite

Three kinds of graphite surfaces facing the positive z region are prepared as follows. In the case of a flat surface (see FIG.1(a).), a single crystalline graphite consists of eight layers where its (0 0 0 1) surface measuring 2.00 x 2.17 nm^2 faces the positive z region. Each layer is a graphene which consists of 160 carbon atoms measuring 2.00 x 2.17 nm^2. The position of the first layer is $z = 11.7$ Å. Two carbon atoms in the eighth graphene layer are fixed during the simulation. In the case of an armchair surface (see FIG.1(b).), a single crystalline graphite consists of six layers where its (1 1 $\bar{2}$ 0) surface measuring 2.01 x 2.17 nm^2 faces the positive z region. Each layer is a graphene which consists of 210 carbon atoms measuring 2.17 x 25.1 nm^2. The position of the top carbon atom is $z = 12.5$ Å. In the case of a zigzag surface (see FIG.1(c).), a single crystalline graphite consists of six layers where its (1 0 $\bar{1}$ 0) surface measuring 2.00 x 2.01 nm^2 faces the positive z region. Each layer is a graphene which consists of 208 carbon atoms measuring 2.00 x 26.8 nm^2. The position of the first layer is $z = 13.4$ Å. One carbon atom located at the bottom in the each graphene layer is fixed during the simulation in the cases of the armchair and zigzag surfaces. In all cases, the center of the single crystalline graphite is set in the center of the simulation box with periodic boundaries only at the x and y directions measuring same size of the surfaces, the interlayer distance of the graphenes layers is arranged at 3.35 Å, and the graphene layers are stacked with an "ABAB" pattern. The carbon atoms obeyed the Maxwell-Boltzmann distribution at 300 K initially.

Hydrogen atoms are injected into the surfaces from the position z = 60 Å parallel to the z direction. The incident position in the x and y direction is determined at random with uniform distribution. The hydrogen atoms are injected at intervals of 0.1 ps and thus the incident flux becomes about 2.5 x 10^{30} m^{-2}s^{-1}. The incident energy E_I determined the initial momentum of the incident particle as $\sqrt{2mE_I}$, where m was the mass of the incident particle, 1 u, 2 u and 3 u for hydrogen, deuterium and tritium atoms, respectively. The initial x and y coordinates of the incident particle were set at random.

2.2. System of a Single Graphene

The MD simulation of hydrogen isotope injection onto a single graphene is performed. The graphene measuring 2.00 x 2.17 nm^2 consists of 160 carbon atoms. The graphene is put on the center of simulation box with the periodic boundary condition in the x and y direction. The initial temperature of the graphene is 0 K. A hydrogen, deuterium or tritium atom is injected perpendicularly to a surface of the graphene. The injection is repeated 200 times varying the incident position which is determined under a uniform distribution for every kind of hydrogen isotope and incident energy. Thereby, we obtain adsorption, reflection and penetration rates as functions of the incident energy for every hydrogen isotope.

2.3. Potential Model

In the present simulation, two types of potential models were used to deal with chemical interaction at short distance and intermolecular interaction at long distance. Chemical interaction was represented by modified Brenner reactive empirical bond order (REBO)

potential in which multi-body force produced complicated molecular structures [7, 8]. In the models, the existence of a covalent bond was judged by the distance between two atoms. C-C and C-H bonds form when the distance between the atoms was less than 2.0 Å and 1.8 Å, respectively. On the other hand, a layer structure is supported by interlayer intermolecular potential which is model on the following natural considerations. If a distance between atoms r is long, the interlayer intermolecular potential accords with van der Waals potential proportional to r^{-6}, while if r is short, the interlayer intermolecular potential causes chemical repulsion represented by multi-body force with special cut-off functions [9]. This interlayer intermolecular potential can keep the interlayer distance of the graphite 3.35 Å and produce the "ABAB" stacking

The time evolution of the equation of motion is solved by the second-order symplectic integration [10]; the time step was 5 x 10^{-18} s. The MD simulations were performed under the *NVE* condition, in which the number of particles (N), volume (V), and total energy (E) were conserved.

3. Result and Discussion

3.1. Dependency of Erosion on Kinds of Graphite Surface

First, we denote the MD simulation injecting hydrogen atoms onto the flat surface of graphite. The MD simulations were performed varying the incident energy from 1 to 30 eV. Though the surface adsorbed many hydrogen atoms, the layer structure of the graphite was maintained. When we continue to inject hydrogen atoms onto the flat surface, the graphene layers were peeled off from the surface one by one, which is called "graphite peeling" (see FIG. 2.). During the graphite peeling, graphene layers under the peeled graphene layer maintained the layer structure of the graphite. We consider as follows. Although the incident hydrogen atoms pressed the graphene layer of the surface to an under graphene layer, interlayer intermolecular force resist being pressed. Consequently the layer structure of the graphite is maintained. Moreover, a covalent bond does not occur between the graphene layers maintained by the interlayer intermolecular force and the binding energy of the interlayer intermolecular force is weaker than that of a covalent bond. Therefore, the graphene layer of the surface easily escapes from a bind by the interlayer intermolecular force when the kinetic energy of the graphene layer increases using adsorption energy of hydrogen atoms. As a result, the graphite peeling occurs.

We note that the layer structure of the graphite does not change to an amorphous structure in case of the flat surface. However, if the graphite includes vacancies, graphite peeling does not occur and amorphization of the graphite occurs [11].

The peeled graphene is broken and then small hydrocarbons are produced. These small hydrocarbons have mainly chain structures in which hydrogen atoms terminate tips of the chains. In our understanding, a hydrocarbon has the chain structure in the environment that the number of carbon atoms in the peeled graphene is grater than that of hydrogen atoms adsorbed by the peeled graphene.

Second, bombardments of hydrogen atoms onto the armchair and zigzag surfaces of graphite were simulated. Armchair and zigzag edges of graphene layers were easily terminated by incident hydrogen atoms. The cause of termination is that the edge of the graphene has dangling bonds. The layered structure of the armchair and zigzag surfaces are also maintained

by the interlayer intermolecular interaction. The graphite peeling does not occur because the graphene layers of the armchair and zigzag surfaces are parallel to the z direction simply.

When an incident hydrogen atom attached the armchair and zigzag edges of the graphene layers, C_2H_2 and H_2 are yielded mainly. Especially, the amount of yielded C_2H_2 on the armchair surface is grater than that on the zigzag surfaces, while the amount of yielded H_2 on the armchair surface is smaller than that on the zigzag surface (see FIG. 3.). This difference is understood as follows.

In the armchair surface, the dynamics of C_2H_2 creation is explained by using FIG. 4 (a). When a hydrogen atom (I) is adsorbed by a carbon atom (III), the incident energy and the binding energy of a C-H bond (i) created between the hydrogen atom (I) and the carbon atom (III) change to the kinetic energy of carbon atoms (IV) and (V). Here, the increase of the kinetic energy of the carbon atom (V) is grater than that of the carbon atom (IV) because the carbon atom (V) located in the incident direction of the hydrogen atom (I) is pushed more strongly than the carbon atom (IV). Therefore, a C-C bond (iii) is broken easily more than a C-C bond (ii). In the same way, when a hydrogen atom (II) is adsorbed by the carbon atom (IV), a C-C bond (iv) is broken. As are result, a C_2H_2, which consists of the atoms (I) to (IV), is yielded from the armchair surface.

On the other hand, the dynamics of H_2 creation on the zigzag surface is explained by using FIG. 4 (b). When a hydrogen atom (VII) is adsorbed by a carbon atom (VIII), the incident energy and the binding energy of a created C-H bond (v) change to the kinetic energy of carbon atoms (IX) and (X). Because positions of the carbon atoms (IX) and (X) are symmetric with the respect to the incident axis of the hydrogen atom (VII), the increase of the kinetic energies of the (IX) and (X) is equal. Therefore, disconnection of the C-C bonds (vi) and (vii) is difficult in the zigzag surface, as compared to the disconnection of the C-C bond (iii) and (iv) in the armchair surface. When a hydrogen atom (XI) approaches to the zigzag surface subsequently, it creates an H-H bond with the hydrogen atom (VII). The C-H bond (v) is broken by use of the incident energy of the hydrogen atom (XI) and the binding energy of the created H-H bond, and then H_2 is desorbed from the zigzag surface. Thus, dominant yielded molecules on the armchair and zigzag surfaces are C_2H_2 and H_2, respectively.

We note these dynamics of C_2H_2 and H_2 creation is observed by use of 3D virtual reality system "CompleXcope" in NIFS. To recognize the atomic motion by a 3D visualisation software rendering on a 2D display is not easy because a behind atom is hidden by front atom in the 2D display. However, the CompleXcope, which can draw the atom in a 3D space, enables us to easily recognize three dimensional positions of atoms. Thus, the CompleXcope is useful device to find important dynamics from the MD simulation.

3.2 Single Graphene Reaction

Investigation of hydrogen atom scattering on a single graphene is important to understand the hydrogen atom bombardment on the layered graphite. Here, we estimate adsorption rate, reflection rate and penetration rate of a hydrogen atom injected into a graphene (see FIG. 5.). In the case of hydrogen atom, dominant interaction varies with the incident energy E_I as follows. Adsorption becomes dominant for 1 eV $< E_I < 7$ eV and has a small peak at $E_I = 22$ eV. Reflection dominates in two ranges, $E_I < 1$ eV and 30 eV $< E_I < 30$ eV. In the case of $E_I > 30$ eV, penetration is dominant.

Here, we estimate the increases of graphene temperature after interacting with a hydrogen atom. Considering conservation of total energy and total momentum in a physical system of a hydrogen atom and a graphene, the increase of graphene temperature is given by

$$\frac{1}{3Nk_b}\left[(E_I - U_0)P_a(E_I) + (1 - \frac{E_r{}'}{E_I})E_I P_r(E_I) + (1 - \frac{E_p{}'}{E_I})E_I P_p(E_I)\right] + O\left(\frac{m}{M}\right)$$

where N is the number of carbon atoms in the graphene, k_b is the Boltzmann constant U_0 is the binding energy of the hydrogen atom on a graphene, $E_r{}'$ and $E_p{}'$ are the kinetic energies of the hydrogen atoms after reflection and penetration, and $P_a(E_I)$, $P_r(E_I)$ and $P_p(E_I)$ are the adsorption rate, reflection rate and penetration rate, respectively [8]. Then, $P_a(E_I)$, $P_r(E_I)$ and $P_p(E_I)$ are already shown in FIG. 5. The ratios of the kinetic energies of the hydrogen atoms after reflection and penetration to the incident energy, $E_r{}'/E_I$ and $E_p{}'/E_I$, can be also calculated from this MD simulation. Thereby, we can obtain the increase of graphene temperature as a function of the incident energy. FIG. 6 illustrates that the increase of the graphene temperature has a peak at about 30 eV. In the consideration that a penetrating hydrogen atom, which has often the incident energy of grater than 30 eV, interacts with the second graphene layer in the flat surface of the layered graphite, a peak increase of temperature of the second graphene layer in the layered graphite shifts to high incident energy as against FIG. 6. Anyway, desorption rate increases as the graphene temperature increases. We consider that this result agrees with that the erosion yield of hydrocarbon has a peak at the incident energy of 40-50 eV [1, 12].

Difference of deuterium and tritium from hydrogen atom in the MD simulation of the single graphene is remarkable rather than in the MD simulation of the layered graphite. For $E_I > 3$ eV in the FIG. 5, as the mass of hydrogen isotope increases, an adsorption rate increases and a reflection rate decreases. On the other hand, a penetration rate doesn't change so much. In the previous work, the following dynamics of a hydrogen atom on the graphene were clarified [8]. When a carbon atom in the graphene adsorbs a hydrogen atom, it needs to change from a sp^2 structure to a sp^3 structure, which is called "overhang". If the stay time during which the hydrogen atom remains on the graphene is longer than the overhang time necessary for overhang, the hydrogen atom is adsorbed. If the relation of the two times is reverse, the hydrogen atom is reflected by the graphene. The stay time becomes long as an incident velocity increases. Then, the adsorption rate increases and the reflection rate decreases. In constant, penetration is that the hydrogen atom goes over a potential barrier of the graphene. Namely, the penetration rate depends on the incident energy and is independent of the incident velocity. In this point of view, a velocity of an incident atom decreases as a mass increases in same incident energy. There, in the case of tritium and deuterium injections, the adsorption rate is grater than that of a hydrogen atom injection, the reflection rate becomes smaller, and the penetration rate does not change.

In the increases of graphene temperature by hydrogen isotope also, the difference from hydrogen atom appears. The peak value of the increases of graphene temperature increases as the mass of the hydrogen isotopes increases (see FIG. 6). This fact expects that the tritium and deuterium bring about yielded hydrocarbons more than the hydrogen atom.

3.3. Hydrogen Retention
The MD simulation of the flat surface of the layered graphite demonstrates hydrogen retention before the graphite peeling starts. The dependency of hydrogen retention on the incident energy is understood by using the result of the MD simulation of a hydrogen atom and a graphene. When the incident energy is 5eV, almost all hydrogen atoms are adsorbed by

the front of the first graphene layer. This adsorption is explained by the result that the adsorption rate on a graphene is dominant at 5 eV. When the incident energy is 15 eV, almost all hydrogen atoms are reflected by the first graphene layer. This reflection is caused by the fact that the reflection rate on a graphene has a peak at 15 eV. However, the deuterium and tritium may be adsorbed by the flat surface at the 15 eV because the reflection rate of the deuterium and tritium on a graphene is smaller than that of hydrogen atom as shown in FIG. 5(b) and (c). When the incident energy is 30 eV, the hydrogen atoms are adsorbed between the first and second graphene layers, that is, the intercalation of hydrogen atoms. This is the following mechanism. The penetration to the first graphene layer is similar to the penetration to a single graphene. By this penetration, the kinetic energy of the hydrogen atom is reduced to the energy at which reflection is dominant on a graphene. Therefore, hydrogen atom repeats to rebound between the first and second graphene layers. The kinetic energy of the hydrogen atom decreases into the energy at which adsorption is dominant on a graphene, and then the hydrogen atom is adsorbed by the first or second graphene layer. We note that in the previous MD simulation without the interlayer intermolecular interaction, the intercalation of hydrogen atom does not occur because the layered structure is hardly maintained under the hydrogen atom bombardment [13].

In the armchair and zigzag surfaces, a part of incident hydrogen atoms goes through from the surface about 5 Å because the planes of graphene layers are parallel to incident direction. In this simulation, the penetrating hydrogen atom flows between graphene layers. When the hydrogen atom get close to the other one, a hydrogen molecule H_2 occur. In our consideration, the graphene layers play a role to diffuse the reaction heat of H_2 production. We note that because a depth of this penetration depends on potential energy for a hydrogen atom on a graphene surface, the hydrogen atom may penetrate more deeply in nature, in which the binding energy of between a hydrogen atom and a graphene is smaller than that of the modified Brenner REBO potential.

4. Summary

The hydrogen atom bombardment onto the three kinds of the layered graphene was investigated by use of the MD simulation with the modified Brenner REBO potential and the interlayer intermolecular potential. On the flat (0 0 0 1) surface, the graphite peeling occurred and the carbon chains were yielded mainly. In the cases of the armchair (1 1 $\bar{2}$ 0) surface and zigzag (1 0 $\bar{1}$ 0) surface, the graphite peeling did not occur. Especially, C_2H_2 was easily generated from the armchair surface, while the zigzag surface generally desorbed H_2. Moreover, the interaction of hydrogen atom on a single graphene was investigated. The adsorption, reflection and penetration rates were calculated and then this data was extended to the increase of the graphene temperature which agrees with the dependence of erosion yield on the incident energy in experiments. As the hydrogen retention is researched, the graphite intercalation of hydrogen appeared in the layered graphite. This hydrogen retention hydrogen retention in the flat surface of the layered graphite is explained by the interaction of hydrogen atom on a single graphene also.

Acknowledgements

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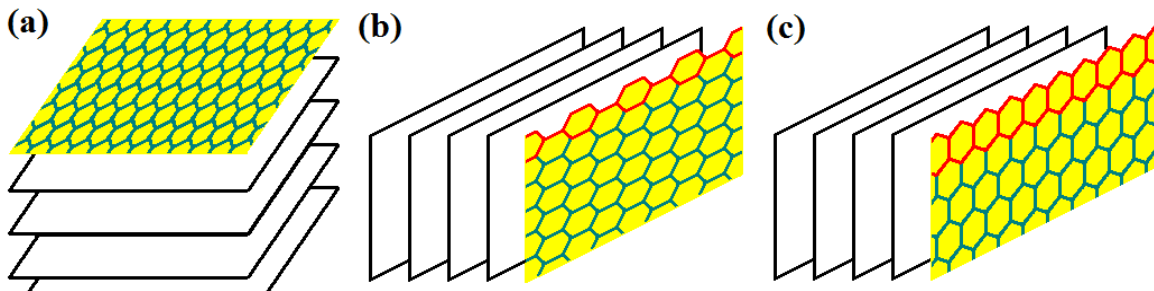

FIG. 1. three kind of graphite surfaces. (a) A flat surface. (b) An armchair surface. (c) A zigzag surface.
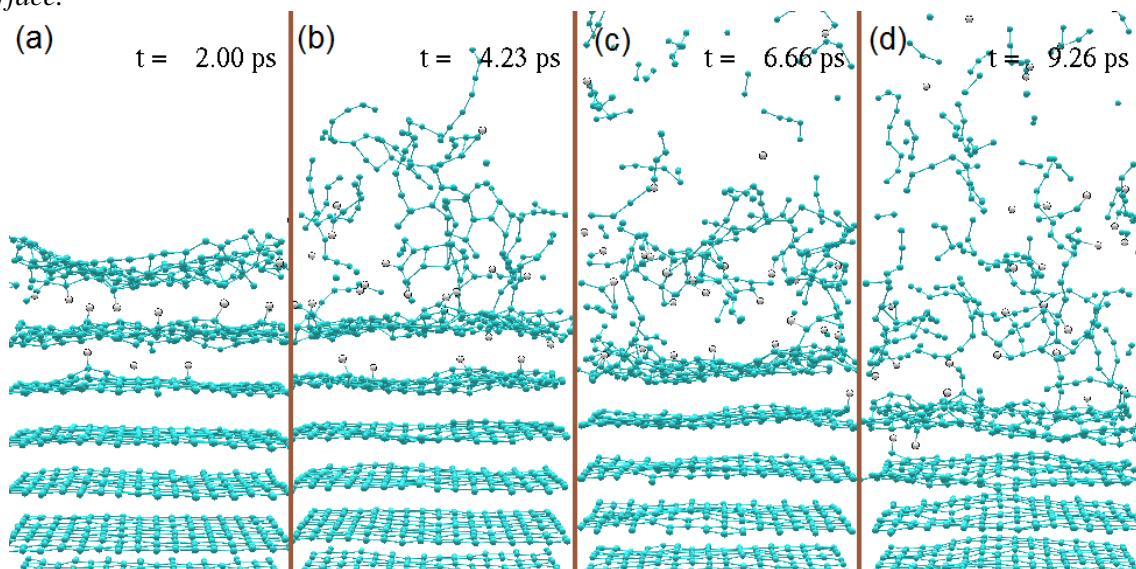

FIG. 2. the snapshots of the MD simulation at the incident energy of 30 eV. White spheres indicate the hydrogen atoms and the green spheres indicate the carbon atoms. From (a) to (d), it is demonstrated that the graphene layers were peeled off one by one, which is called the graphene peeling. This graphene peeling is particular to the layer structured graphite kept by the interlayer intermolecular interaction.
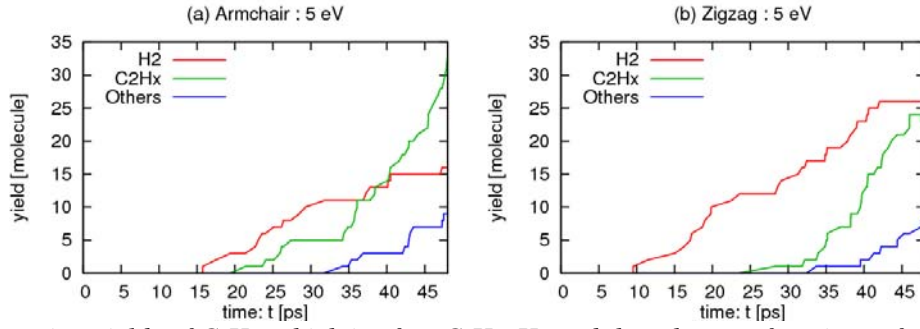
FIG. 3. sputtering yields of C_2H_x, which is often C_2H_2, H_2 and the others as functions of time.
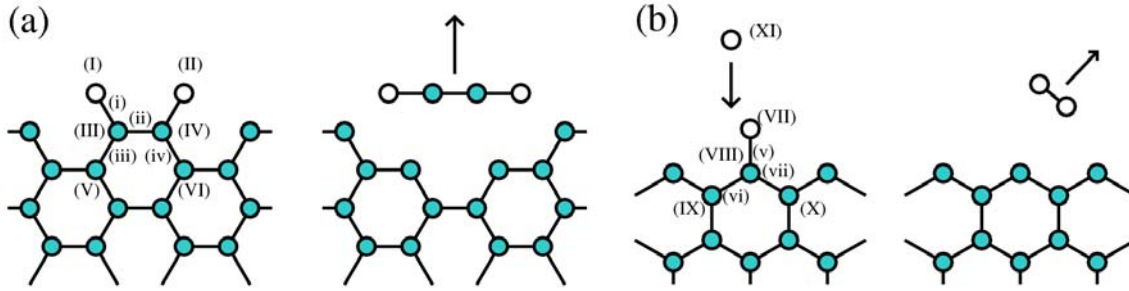

FIG.4. (a) the mechanism of C_2H_2 creation on the armchair surface. (b) the mechanism of H_2 creation on the zigzag surface.
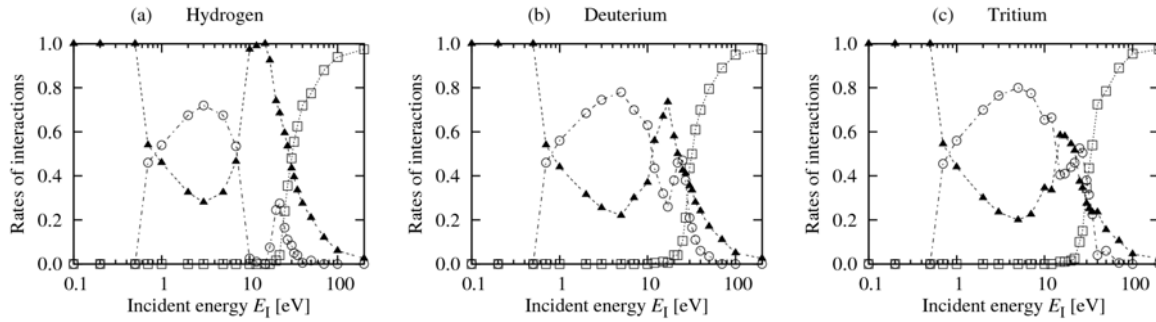

FIG.5. adsorption, reflection and penetration rates as functions of the incident energy. Figures (a-c) indicate the cases of hydrogen, deuterium and tritium atoms, respectively.
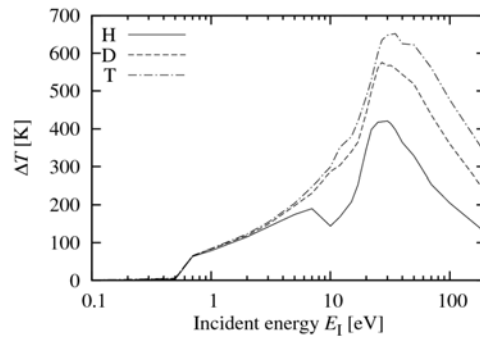

FIG.6. the increase of the graphene temperature. The solid, dashed, dash-dotted lines indicate the cases of hydrogen, deuterium and tritium atoms, respectively.