Effects of Hydrogen Incorporation in the Formation of Hydrogenated Diamond-like Carbon Films

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Abstract. The formation process of sp\textsuperscript{3} hybridized carbon networks (i.e., diamond-like structures) in hydrogenated diamond-like carbon (DLC) films has been studied with the use of molecular dynamics (MD) simulations. A recent study [Y. Murakami, S. Horiguchi, and S. Hamaguchi, Phys. Rev. E. (2010) in press] has shown that a sufficient supply of hydrogen in the form of hydrocarbon species CH\textsubscript{x} as deposition precursors significantly enhances the formation of sp\textsuperscript{3} hybridized bond structures in the deposited film. In this study, we have examined the role of hydrogen in such deposition processes by simulating the cases where carbon and hydrogen atoms are supplied to the surface separately. It has been found that, in such a case, the rate of sp\textsuperscript{3} bond formation is significantly lower than that in the corresponding case of CH\textsubscript{x} injections. The result suggests that energetic hydrogen atoms present in the vicinity of the incident carbon atoms promote the formation of $\sigma$ bonds (and therefore sp\textsuperscript{3} bonds) among carbon atoms by increasing the rates of $\pi$ bond termination and hydrogen abstraction reactions.

1. Introduction
Amorphous carbon with a high content of sp\textsuperscript{3} structures is often called diamond-like carbon (DLC) and known to have extraordinary material properties such as high mechanical hardness, high wear resistance, low friction coefficients, high chemical inertness, good infrared (IR) transparency, high electrical resistivity, good field emission properties, and low dielectric coefficients [1-7]. For example, DLC is used widely as protection layers for data storage disks and magnetic recording heads.

Characteristics of DLC films are generally determined by the amount of sp\textsuperscript{3} hybridized bonds present in the films [2]. In the present study, we examine sp\textsuperscript{3} hybridized bond formation mechanisms in hydrogenated amorphous carbon (a-C:H) deposition processes. In recent studies [8,9] based on numerical simulations, it has been shown that the presence of a sufficient amount of hydrogen in an amorphous carbon film being deposited significantly enhances the formation of sp\textsuperscript{3} hybridized bond structures if the incident (hydro)carbon beam has a sufficiently high kinetic energy. In these studies, hydrogen was supplied to the surface in the form of hydrocarbon species CH\textsubscript{x} as deposition precursors. In the present study, we simulate the cases where carbon and hydrogen atoms are supplied to the surface separately in order to clarify the role of hydrogen in such deposition processes.

As a tool for the study, we use classical molecular dynamics (MD) simulation, by which dynamics of individual atoms may be examined in detail. In this work, we examine the initial phase of carbon film deposition by numerically simulating injection processes of carbon, hydrogen, or hydrocarbon
atoms/clusters into amorphous carbon (a-C) films that are initially hydrogen-free. These results may be compared to the results given in Ref. [9], where injection processes of CH and CH$_3$ were examined. It is of our special interest here whether hydrogen injected separately from the incident carbon atoms can also enhance the formation of sp$^3$ structures in a carbon deposition process.

The rest of the paper is arranged in the following manner. We first briefly present our MD simulation scheme in the next section. In Sec. 3, simulation results are presented and discussed. The conclusions are given in the final section.

2. Molecular Dynamics Simulation
In classical MD simulations, trajectories of all atoms in the system are obtained from the integration of Newton’s equations of motion [10-13] and macroscopic physical quantities, such as deposition rates and sputtering yields, may be obtained from proper averaging of corresponding microscopic quantities. Atomic interactions in classical MD simulations are predetermined and the interatomic potential functions used in this study are multi-body potential functions that are the same as those used in Refs. [8] and [9]. More details on the functions may be found in Ref. [11].

The model substrate used in the simulation is a hydrogen-free amorphous carbon (a-C) cube with an edge length of about 2 nm. It consists of approximately 800 carbon atoms that were initially arranged at random positions in the cube and then brought to thermal equilibrium at 300 K by MD simulations of canonical ensemble (with constant temperature and density). Its mass density is about 2.0 g/cm$^3$, which is typical for a-C. The model substrate consists mainly of sp$^2$ hybridized bonds; the ratio of the number of sp$^3$ carbon atoms to that of sp$^2$ atoms in the model substrate is about 0.4%.

The periodic boundary conditions are imposed in the lateral directions and therefore the model substrate represents an infinitely wide flat thin film with a thickness of about 2 nm. Atoms in the 0.4 nm thick bottom layer of the substrate are set immobile lest the substrate drift downward when its top surface is subjected to beam injection.

In this work, the beam species that we have chosen to examine are C, H, and CH$_3$. It has been known that CH$_3$ is the most abundant radical species in methane plasmas that are often used for a-C:H deposition in Plasma-Enhanced Chemical Vapour Deposition (PECVD) processes [14-17]. Methyl ion CH$_3^+$ is known to form one of the largest ion fluxes emitted from methane plasmas [15]. Energetic beams simulated in this work are considered to represent ion beams. However, all interatomic forces used in the simulations are those for charge neutral species for the sake of simplicity.

The sequence of deposition simulations is the following [8-13]. A single simulation cycle starts with an injection of the selected species (such as CH$_3$) at a predetermined kinetic energy into the substrate surface. The substrate is set in thermal equilibrium at 300 K. The initial lateral position of the injected species is randomly selected and its initial height is set to be about 1 nm above the substrate surface. The incident angle is normal to the substrate surface. The trajectories of all atoms are then obtained from the integration of Newton’s equations of motion under the condition of constant total energy, i.e., microcanonical conditions, for 0.8 ps. The numerical time integration is based on the velocity Verlet algorithm. The system is then rapidly cooled and equilibrated at the initial temperature (300 K) during the following 0.2 ps to remove the excess heat from the system. The next simulation cycle then starts with a new particle injection, as in the first cycle. In the MD simulation study presented here, such simulations cycles are typically repeated 500-800 times, which corresponds to the beam dose (i.e., fluence) of 1.25×10$^{16}$ to 2.0×10$^{16}$ cm$^{-2}$.

3. Simulation results
In this work, we performed four different sets of simulations in order to clarify the formation mechanisms of sp$^3$ bonds in the deposited carbon films. Hardness and other industrially useful characteristics of a DLC film is determined by the sp$^3$ carbon content in the film. Table 1 shows the four different simulation conditions employed in this work.

In the simulation case denoted by Condition I, carbon atoms are injected 800 times into the model substrate. As discussed above, in each injection cycle, the MD simulation is run under the
microcanonical condition for 0.8 ps after a single carbon atom C is released from a location above the model substrate surface with a kinetic energy of 50 eV in the direction normal to the substrate surface. The system is then cooled for 0.2 ps to 300 K. Similarly, in the case denoted by Condition II, CH₃ (instead of C) atomic clusters are injected into the model substrate surface with the same conditions.

| Table 1. Conditions for simulations presented in this article. |
|---------------------------------------------------------------|
| Conditions     | I  | II | III | IV  |
| Species        | C  | CH₃| C   | H  |
| Number per     | 1  | 1  | 1   | 3  |
| injection cycle| 800| 800| 660 | 500|
| kinetic energy | 50 | 50 | 40  | 3.3|
| (eV) per species|    |    |     | 0.025|
| Number of      |    |    |     |     |
| Injection cycles| 800| 800| 660 | 500|

In Condition III, the single simulation cycle consists of two separate sets of injections. In the first set of injection, as in Condition I, a single C atom is injected with a kinetic energy of 40 eV. The system is under the microcanonical condition for 0.8 ps and then cooled for 0.2 ps to 300 K, as in the Conditions I and II. Then in the second set of injections, three H atoms are injected simultaneously from random locations above the substrate surface with a kinetic energy of 3.3 eV for each. MD simulations are run under the microcanonical conditions for 0.8 ps and then cooled for 0.2 ps to 300 K, as in the first set. In Condition III, the total kinetic energy of C and three H atoms is 50 eV, which is the same kinetic energy of CH₃ of Condition II. The main difference between Condition II and Condition III is that, in Condition III, injected hydrogen atoms may not be in the vicinity of the injected C atom as their locations are selected randomly.

In Condition IV, 200 H atoms are supplied simultaneously to the substrate surface with sufficient low energy in a single injection cycle. The other conditions are similar to those in Conditions I and II.

Figure 1 shows the fully carbon terminated sp³ fractions as functions of injection dose of C atoms under the Conditions I (denoted by the thin solid curve), II (broken curve), and III (thick solid curve). Here the “fully carbon terminated sp³ fraction” means the fraction of fully carbon terminated sp³ C atoms (each of which is bonded with 4 other C atoms only, not more and not less) for all deposited C atoms. This fraction represents the “diamond-likeness” of the deposited film. It should be noted that when the dose is small (i.e., the number of all deposited C atoms is small), the fractions given in Fig. 1 is statistically meaningless. However Fig. 1 shows that there are clear differences among the three cases when the dose is sufficiently large. The case of Condition II is the same as that shown in Fig. 6 of Ref. [9].

It is clearly seen in Fig. 1 that fully carbon terminated sp³ structures are more efficiently formed under Condition II or III than Condition I, in which no hydrogen is provided to the surface. It indicates the importance of the role of hydrogen for efficient formation of diamond-like structures in carbon deposition processes.

Figure 1 also shows that a relatively large sp³ fraction is obtained as the injection does of CH₃ increases under Condition II whereas the sp³ fraction remains relatively small under Condition III, in which the same number of C and H atoms with the same kinetic energy for each atom are supplied to the substrate surface. Since a 50 eV CH₃ atomic cluster tends to break up when it hits the surface, one might expect that a similar process would occur after the injected C atom hits the substrate surface in both Conditions II and III. The major difference between these two cases is that, in Condition II, broken up H atoms may remain still in the vicinity of the injected C atom and therefore contribute to
the formation of C-to-C $\sigma$ bonds by bond scissions and/or hydrogen abstraction due to their relatively high kinetic energies.

For Condition IV, on the other hand, very few sp$^3$ structures have been observed to be formed. Therefore the sp$^3$ fraction under Condition IV is not given in Fig. 1.

Figure 2 shows depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp$^2$ bond density at various beam carbon doses under Condition II, obtained from MD simulations. Here the sp$^2$ bond means a carbon bond that contains a (partial) $\pi$ orbital, such as the carbon bond of graphite. The horizontal axis represents the film thickness measured from the bottom of the model substrate. Each curve represents the density profile at the specified carbon dose. It is seen that, under Condition II, the C-to-C $\sigma$ bond increases rapidly in the region below the top surface whereas the carbon sp$^2$ bond density in the same region gradually decreases. As seen in Fig. 1, the sp$^3$ fraction starts to increase at around $1.2 \times 10^{16}$ cm$^{-3}$ of carbon dose. Around this dose, the rapid decrease of carbon sp$^2$ bonds in the region also occurs, as indicated in Fig. 2(b). The decrease of sp$^2$ bond structures indicates that hydrogen atoms are sufficiently supplied to the substrate to the extent that a large number of $\pi$ bonds there have been terminated by the supplied hydrogen atoms. Therefore we conjecture that, once the surface and subsurface regions are nearly saturated with hydrogen, energetically injected C atoms have higher chances of converting two carbon-to-hydrogen (C-H) bonds to a single carbon-to-carbon (C-C) $\sigma$ bond in the region by promoting hydrogen abstraction reactions.

To compare the sp$^3$ formation processes between Conditions II and III, we present Fig. 3, where the depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp$^2$ bond density at various beam carbon doses under Condition III. Although the $\sigma$ bond density increases near the surface region, as in the case of Fig. 2 (a), the sp$^2$ bond density also increases in the same region. This is the trend opposite to that seen in Fig. 2(b), in which the sp$^2$ bond density decreases as the injection dose increases. At this moment, it is not clear why the sp$^2$ bond density increases under Condition III. It is possible that hydrogen atoms injected at a few eV may convert freshly formed sp$^3$ structures to sp$^2$ structures. However, abundant hydrogen supply tends to break $\pi$ bonds and therefore could reduce the number of sp$^2$ structures, as we have seen in Fig. 1.

Figure 4 also shows the depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp$^2$ bond density at various hydrogen doses under Condition IV, where low-energy H atoms are supplied to the surface without carbon injections. It is clearly seen that sp$^2$ bond structures of the initial substrate are
reduced in this process, as one expects. It is also seen that the C-to-C $\sigma$ bond (i.e., single bond) density increases near the surface, which is a mere consequence of conversion of covalent bonds with $\pi$ orbitals to pure C-to-C $\sigma$ bonds due to breakup of the $\pi$ bonds by supplied hydrogen.

Figure 2. The depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp$^2$ bond density at various beam doses in Condition II, i.e., the case of 50 eV CH$_3$ beam incidence, obtained from MD simulations. The horizontal axis represents the film thickness measured from the bottom of the model substrate [9].

Figure 3. The depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp$^2$ bond density at various beam doses in Condition III, i.e., the separate injections of C at 40 eV and three H atoms at 3.3 eV each, obtained from MD simulations.
Figure 4. The depth profiles of the (a) C-to-C $\sigma$ bond density and (b) carbon sp² bond density at various beam doses in Condition IV, i.e., injections of H atoms at low energy, obtained from MD simulations.

Figure 5. The depth profile of fully carbon terminated sp³ C atoms at a dose of $4.0\times10^{16}$ cm$^{-2}$ under Condition IV (depicted by the grey curve denoted by “sp³ C” and its value is given on the right scale), obtained from MD simulations. The profiles of C atoms including sp³ C atoms in the initial (thick solid curve) and final (thin solid curve) states as well as the profile of deposited H atoms (dotted curve) are also plotted. Their values are given on the left scale. It is clearly seen that the number density of sp³ C atoms formed in this process is significantly smaller than the total carbon density of the substrate.
Even under Condition IV, a very small number of fully carbon terminated sp³ bonds are formed. Shown in Fig. 5 are the depth profile of fully carbon terminated sp³ C atoms at a dose of 4.0×10¹⁶ cm⁻² under Condition IV (depicted by the grey curve denoted by “sp³ C” and its value is given on the right scale), the profiles of C atoms including sp³ C atoms in the initial (thick solid curve) and final (thin solid curve) states, and the profile of deposited H atoms (dotted curve). The values for the C and H densities are given on the left scale. It is clearly seen that the number density of sp³ C atoms formed in this process is significantly smaller than the total carbon density of the substrate.

4. Concluding remarks
We have examined the formation processes of fully carbon terminated sp³ bonds under four different conditions summarized in Table 1, using MD simulations. It has been observed in the simulations that the presence of hydrogen in carbon deposition processes promotes the formation of sp³ bonds in general. However, injections of carbon in the form of CH₃, rather than C and H atoms separately under similar conditions, exhibit the sp³ formation at much higher rates. Although the exact cause for the enhanced rate of sp³ bond formation has not been clear yet, the observations suggest that the presence of hydrogen with a kinetic energy of a few eV in the vicinity of the incident C atoms significantly promote the formation of the C-to-C σ bonds by bond scissions and/or hydrogen abstraction. More detailed examination of the role of energetic hydrogen randomly injected into a-C films in the sp³ formation processes is deferred to a future study.

Acknowledgments
The work is partially supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan. The authors are also grateful for the technical support for computer simulations by Mr. M. Isobe of Osaka University and Dr. M. Yamashiro of Nihon University.

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