Formation and Classification of Amorphous Carbon by Molecular Dynamics Simulation

Atsushi M. Ito1,†, Arimichi Takayama1, Seiki Saito2, and Hiroaki Nakamura1,2

1 Department of Helical Plasma Research, National Institute for Fusion Science, Toki, Gifu 509-5292, Japan
2 Department of Energy Engineering and Science, Nagoya University, Nagoya 464-8602, Japan
E-mail: ito.atsushi@nifs.ac.jp
Received May 14, 2012; accepted August 18, 2012; published online January 21, 2013

By using molecular dynamics simulation, the formation mechanisms of amorphous carbon in a particular sp^3-rich structure were researched. The problem that reactive empirical bond order potential cannot represent amorphous carbon properly was resolved in the transition process from graphite to diamond by a high pressure and the deposition of amorphous carbon thin films. Moreover, a new potential model, which is based on the electron distribution simplified as a point charge, was developed by using the downfolding method. As a result, the molecular dynamics simulation with the new potential could demonstrate the transition from graphite to diamond at the pressure of 15 GPa, which agrees with an experimental report and the deposition of sp^3-rich amorphous carbon. © 2013 The Japan Society of Applied Physics

1. Introduction

There are many amorphous materials in the world. In the past, almost all of them were classified as “amorphous” just because they do not have crystalline structures. However, amorphous materials with different structures and properties in spite of having the same constituent atomic elements have been found. The reason for the structural diversity of amorphous carbon materials is that an sp^3 structure, which is a metastable state, is as stable as an sp^2 structure in carbon. For this reason, one important parameter to classify amorphous carbon materials is the sp^3/sp^2 ratio, which is the ratio of the number of sp^3 carbon atoms to that of sp^2 carbon atoms. Actually, in the best-known classification of amorphous carbon materials proposed by Jacob and Moller,1) and Robertson,2) the sp^3/sp^2 ratio was selected as a classification parameter with hydrogen content rate. However, amorphous carbon materials that have similar sp^3/sp^2 ratios and hydrogen contents can have different physical properties such as strength. The classification by these two parameters is, therefore, not sufficient to understand amorphous carbon materials. In other words, if a more detailed classification is obtained, it can lead to the discovery of new amorphous carbon materials with functional physical properties such as frictional, electric conduction, and semiconductor properties. Aiming to establish a new classification for amorphous carbon materials, we have investigated the relationship between the atomic geometries and formation processes of amorphous carbon materials with molecular dynamics (MD) simulation. MD simulation is a powerful method because it can demonstrate amorphous structures in the atomic scale directly. Our previous research clarified that the amorphous carbon materials created by deposition or annealing differ in the orientation of covalent bonds, although they are similar in density, sp^3/sp^2 ratio, and radial distribution function.3) It follows from this that to clarify the difference in amorphous carbon materials, their formation processes should be understood simultaneously.

The purpose of this study is to investigate amorphous carbon materials with sp^3-rich structures. In general, almost all carbon materials have sp^2-rich structures, and diamond with sp^3-rich structure should be generated in a high pressure environment. However, diamond-like carbons (DLCs) are created by deposition at low pressures, and they also have sp^3-rich structures. It is not clear how DLCs can have many sp^3 carbon atoms in an amorphous structure.

In a previous work, we investigated amorphous carbon deposition by using MD simulation with the second generation reactive empirical bond order (REBO2002) potential.4,5) As a result, the relationship between the deposition and H/C ratios of incident atoms onto a surface was clarified, and this relationship agrees with experimental results.6) After that, using a similar MD simulation technique, we have attempted to clarify the difference between the formation processes of sp^2- and sp^3-rich amorphous carbon deposits. Simultaneously, we have tackled the MD simulation of a graphite-to-diamond transition at a high pressure because the transition is regarded as a structural change from a pure sp^2 structure of graphite to a pure sp^3 structure of diamond via sp^2- and sp^3-rich amorphous carbon structures. However, in those MD simulations, we encountered the two obstacles that sp^3-rich amorphous carbon deposits cannot be created, and graphite cannot change into diamond at pressures higher than 100 GPa, where the experimental transition pressure was reported to be about 15 GPa.7) The reason for these problems is that the empirical function forms in the REBO2002 potential have trouble representing the potential energy of amorphous structures.

Here, we note the empirical function forms in the REBO2002 potential. In general, almost all models of potential for the MD simulation of a real atomic system, especially those in which the dominant interaction is covalent bonding, are classified as the “bond order (BO)” potential. The BO potential is composed of the functions of the length of a covalent bond, the bond angle, which is the angle between two adjacent covalent bonds, the dihedral angle, which is the angle between two adjacent planes formed by three continuous covalent bonds, and so on. As an extension for the BO potential to treat new connecting and cutting of covalent bonds, Brenner et al.8) added the term of functions of the number of surrounding atoms within a cutoff length. This surrounding term represents the energy difference among molecular structures empirically, and then the potential energy of a reaction intermediate molecule was given by the interpolation of the energies of molecules before and after the reaction, which is called the reactive empirical bond order (REBO) potential. The REBO potential...
is most often employed in the study of carbon nanomaterials. The second-generation model of REBO potential (REBO2002), which was improved over a period of twelve years by Brenner et al.,\(^4\) can calculate reasonable energies for almost all carbon and hydrocarbon molecules.

Thus, the REBO2002 potential well represents stable molecular and lattice structures in terms of potential energy. However, metastable structures such as amorphous structures are hardly considered in the REBO2002 and general BO potentials. Therefore, in the present work, we propose a new potential model for amorphous carbon materials. The new potential model is based on the consideration of the electron distribution such as molecular orbitals. That is, the new potential model is not classified as the BO potential. Consequently, in the MD simulation with the new potential model, the creation of sp\(^3\)-rich amorphous carbon in the deposition process and the graphite-to-diamond transition at the pressure of 15 GPa could be successfully simulated.

### 2. Electron Order Potential

#### 2.1 Potential function form

As a function form of the new potential, BO- and REBO-type functions are not employed. The total potential energy \(U_{\text{tot}}\) is composed of nucleus–nucleus repulsive energy \(U_{\text{nn}}\), nucleus–electron attractive energy \(U_{\text{ne}}\), and electron–electron repulsive energy \(U_{\text{ee}}\) as

\[
U_{\text{tot}} = U_{\text{nn}} + U_{\text{ne}} + U_{\text{ee}}. 
\]

The nucleus–nucleus repulsive energy \(U_{\text{nn}}\) has a function form of screened Coulomb interaction given by

\[
U_{\text{nn}} = \frac{1}{2} \sum_{i,j \neq i} K_{\text{nn}} \frac{Q_i Q_j}{r_{ij}} \exp(-a_{\text{nn}} r_{ij}) f_{\text{nn}}(r_{ij}), 
\]

where \(\sum_{i,j \neq i}\) means summation in terms of pairs of \(i\)-th and \(j\)-th nuclei, \(Q_i\) and \(Q_j\) are core charges of nuclei, which are screened by core electrons, \(r_{ij} = |r_i - r_j|\) is the distance between the \(i\)-th and \(j\)-th nuclei, and \(f_{\text{nn}}(r_{ij})\) is a cutoff function. The details of cutoff functions are described later.

To construct the nucleus–electron attractive energy \(U_{\text{ne}}\) and electron–electron repulsive energy \(U_{\text{ee}}\), the electron distribution such as that due to molecular orbitals is considered. Of course, the electron distribution is simplified as a point charge located at the position of atom (nuclei) \(r_i\) and the center position between pair atoms \(\vec{r}_{ij} = (r_i + r_j)/2\). When the \(i\)-th and \(j\)-th atoms are close, electric charge transfer from the position of the \(i\)-th atom to the center position between the \(i\)-th and \(j\)-th atoms is defined by

\[
q_i(r_{ij}) = q_i^o + \sum_{j \neq i} q_j(r_{ij}), 
\]

where \(q_i^o\) is the number of valence electrons depending on the atomic element of the \(i\)-th atom.

The nucleus-electron attractive energy \(U_{\text{ne}}\) is divided into four terms as follows:

\[
U_{\text{ne}} = U_{\text{ne}}^o + U_{\text{ne}}^{\text{es}} + U_{\text{ne}}^{\text{ss}}. 
\]

The term \(U_{\text{ne}}^o\) is the attractive energy between the nucleus and the nearest shared electron pair defined by

\[
U_{\text{ne}}^o = - \sum_{i,j \neq i} K_{\text{ne}}^o \exp(-a_{\text{ne}} r_{ij}) q_i(r_{ij}) q_j(r_{ij}), 
\]

where \(K_{\text{ne}}^o\) is a cutoff function. The second-nearest unpaired electron defined by

\[
U_{\text{ne}}^{\text{ss}} = - \sum_{i,j \neq i} K_{\text{ne}}^{\text{ss}} \exp(-a_{\text{ne}}^2 r_{ij}) q_i(r_{ij})^2 q_j(r_{ij}), 
\]

where \(K_{\text{ne}}^{\text{ss}}\) is a cutoff function. The third term \(U_{\text{ne}}^{\text{es}}\) is the attractive energy between the nucleus and the nearest unpaired electron defined by

\[
U_{\text{ne}}^{\text{es}} = - \sum_{i,j \neq i} K_{\text{ne}}^{\text{es}} Q_i q_i^o(r_{ij}), 
\]

where the electric charge of unpaired electrons \(q_i^o(r_{ij})\) is given by Eq. (5). The nearest unpaired electron is located at the same position as the nucleus. The term \(U_{\text{ne}}^{\text{es}}\) is the attractive energy between the nucleus and the second-nearest unpaired electron defined by

\[
U_{\text{ne}}^{\text{es}} = - \sum_{i,j \neq i} K_{\text{ne}}^{\text{es}} Q_i q_i^o(r_{ij}) q_j(r_{ij}), 
\]

where \(K_{\text{ne}}^{\text{es}}\) is a cutoff function. The second-nearest unpaired electrons are located at the same position as that of the second-nearest nucleus, the distance between the nucleus and the second-nearest unpaired electrons is the same as that between a pair of nuclei.

The electron–electron repulsive energy \(U_{\text{ee}}\) is modeled by using the electric charge of a shared electron pair determined by Eq. (3) and that of unpaired electrons determined by Eq. (5) similarly to \(U_{\text{ne}}\). The electron–electron repulsive energy \(U_{\text{ee}}\) is composed of the following three terms:

\[
U_{\text{ee}} = U_{\text{ee}}^p + U_{\text{ee}}^{\text{ss}} + U_{\text{ee}}^{\text{es}}. 
\]

The first term \(U_{\text{ee}}^p\) is the repulsive energy between two electrons in a shared pair defined by

\[
U_{\text{ee}}^p = \frac{1}{2} \sum_{i,j \neq i} K_{\text{ee}}^p q_i(r_{ij}) q_j(r_{ij}). 
\]

The second term \(U_{\text{ee}}^{\text{ss}}\) is the repulsive energy between two adjacent shared electron pairs defined by

\[
U_{\text{ee}}^{\text{ss}} = \sum_{i,j \neq i, k \neq j} K_{\text{ee}}^{\text{ss}} \exp(-a_{\text{ee}}^3 |r_i - r_{ik}|) [q_i(r_{ij})^2 q_j(r_{ij}) + q_i(r_{ij}) q_j(r_{ij})]. 
\]

The third term \(U_{\text{ee}}^{\text{es}}\) is the repulsive energy between a shared electron pair and the nearest unpaired electrons defined by
\[ U_{ne} = \sum_{i,j,l} K_{ne}^{kl} \exp(-a_{ne}^{kl} |\mathbf{r}_{ij} - \mathbf{r}_l|) \]
\[ \times [q_i(r_{ij}) + q_j(r_{ij})]q_l(|\mathbf{r}|). \] (14)

There are three cutoff functions, \( f_{nn}, f_{ne}^2, \) and \( f_{ne}^4 \), in the above definitions. In the present work, all cutoff functions are unified by using Eq. (4) as
\[ f_{nn}(r) = f_{ne}^2(r) = f_{ne}^4(r) = f_{0} \left( \frac{r - R_{0}}{\epsilon_{nn}} \right). \] (15)

Except for the nucleus–nucleus repulsive energy \( U_{ne} \) in Eq. (2), all the terms have no Coulomb potential form. The reason for this is that \( U_{ne} \) and \( U_{ee} \) are regarded as the interaction energy of not so much a classical electron particle but rather the electric charge distribution due to quantum electron orbitals in the present model. Although the potential model in the present work is composed of only the above terms, a higher quality potential model can be created by adopting nucleus-electron attractive and electron-electron repulsive terms between more distant positions.

2.2 Downfolding method

An ideal potential model should be able to calculate the proper interatomic interaction energy in an arbitrary atomic geometry. In other words, a potential model that can calculate interatomic interaction energy in many types of atomic geometry with accuracy is regarded as a good model. Currently, the development of quantum chemistry, which is represented by the density functional theory (DFT), has made it possible to calculate the interatomic interaction energy with a high degree of accuracy. Then, by converging the parameters in the potential function so as to reduce the difference between the interatomic interaction energies calculated using the potential model and DFT in many atomic geometries, we can obtain a good potential model. Yoshimoto proposed the downfolding method to develop a potential model from this point of view.9 In the present work, the parameters in the function form given in Sect. 2.1 are optimized by the downfolding method as follows.

Potential is, of course, a function of atomic geometry \( \{r\} = \{r_1, r_2, \ldots\} \). If parameters in the potential function are regarded as variables, the potential is also a function of the parameters. The parameters in the potential function are described as \( \{\alpha\} = \{a_1, a_2, \ldots\} \), and the potential function is described as \( U(\{r\}, \{\alpha\}) \). The variance of difference between interatomic interaction energies calculated using the potential model and DFT in terms of \( N \) types of sample atomic geometries is given by
\[ \Phi = \frac{1}{N} \sum_{i} [U(\{r\}_i, \{\alpha\}) - E_{\text{ref}}(\{r\}_i)]^2, \] (16)
where \( \{r_i\} \) means the i-th sample atomic geometry and the reference energy \( E_{\text{ref}}(\{r\}_i) \) is the interatomic interaction energy calculated by using DFT. To reduce \( \Phi \), the parameters \( \{\alpha\} \) are optimized.

One way to optimize the parameters \( \{\alpha\} \) is to solve the following evolution equation for a virtual time \( t \):
\[ \frac{d\alpha_i}{dt} = -\epsilon \frac{\partial \Phi}{\partial \alpha_i} = -\frac{2c}{N} \sum_{i} \frac{\partial U(\{r\}_i, \{\alpha'\})}{\partial \alpha_i} \times [U(\{r\}_i, \{\alpha'\}) - E_{\text{ref}}(\{r\}_i)]. \] (17)

In an actual operation, how to prepare the sample atomic geometries is important. Yoshimoto9 proposed that the sample atomic geometries are selected from an animation snapshot in a preliminarily performed MD simulation with the potential function \( U(\{r\}, \{\alpha\}) \), which employs temporary parameters \( \{\alpha\} \). For example, if the preliminary MD simulation is executed in a canonical ensemble scheme, the sample atomic geometries are generated according to a canonical distribution. Yoshimoto adopted a multicanonical ensemble scheme as a preliminary MD simulation. Moreover, the iteration of the above sequence of the downfolding method, replacing temporary parameters \( \{\alpha\} \) with the optimal parameters given by the previous sequence, is an effective technique to obtain more optimal parameters. This iteration is also effective for preventing the parameters from being trapped in a local minimum.

In the present work, the optimized parameters \( \{\alpha\} \) in the above sequence correspond to fifteen parameters \( \{O, K_{nn}, a_{nn}, K_{ne}^{kl}, a_{ne}^{kl}, K_{ee}^{kl}, a_{ee}^{kl}, K_{ne}^{kl}, a_{ne}^{kl}, K_{ee}^{kl}, a_{ee}^{kl}, K_{ne}^{kl}, a_{ne}^{kl}, K_{ee}^{kl}, a_{ee}^{kl}, K_{ne}^{kl}, a_{ne}^{kl}, K_{ee}^{kl}, a_{ee}^{kl}\} \) in the function form defined in Sect. 2.1. Sample atomic geometries were created by the three types of preliminary MD simulation with the REBO2002 potential. One third of sample atomic geometries were selected from graphite structures vibrating at high temperatures, the next one third of sample atomic geometries were selected from diamond structures similarly, and the other one third of sample atomic geometries were selected from amorphous structures obtained by pressing graphite in the preliminary MD simulation. The reference energies \( E_{\text{ref}}(\{r\}_i) \) for the sample atomic geometries were calculated with the “Open source package for Material eXplorer” (OpenMX), which is numerical software based on DFT.10,11 The generalized gradient approximation (GGA) with a Perdew–Burke–Ernzerhof (PBE) functional12 was employed as an exchange–correlation potential. Linear combinations of pseudo-atomic orbitals (LCPAOs)13,14 norm conserving pseudo-potentials15 and projector expansions16 were used for approximation for core electrons and nuclei. Electron orbitals were represented by numerical orbitals with pseudo-atomic localized basis functions.

As a result, the optimal parameters were obtained, where the iteration of the downfolding method was not performed in the present work. The optimal and fixed parameters are shown in Table I.

3. Application

3.1 Transition from graphite to diamond

The first result by the new potential was that the transition from graphite to diamond could be well imitated by MD
simulation. In this MD simulation, it was observed that the lattice structure changes from a graphite structure to a diamond structure as the pressure of the system increases gradually. The system had 24 carbon atoms, which initially formed the graphite structure composed of three graphene layers with an “ABC” stacking form. The simulation box was under the periodic boundary condition. The pressure of the system was controlled by the Andersen barostat method, where the setting pressure increased from 3 to 15 GPa in the first 4 × 10^{-12} s, and then it was kept at 15 GPa during the next 4 × 10^{-12} s. The size of the simulation box was initially 0.492 × 0.426 × 1.004 nm^2, and it was changed according to the pressure of the system on the basis of the Andersen barostat method. The different point from the original Andersen barostat method was that the pressure and size of the simulation box were controlled independently for each of the x, y, and z directions. The temperature of the system was also controlled by the Langevin thermostat method, in which the temperature was 1000 K and the friction coefficient was 1.0 × 10^{14} s^{-1}. The time step of the MD simulation was 4.0 × 10^{-10} s. After 2.0 × 10^5 steps, the MD simulation was finished.

Figure 1 shows the change in pressure in the MD simulation. From this figure, it was confirmed that the pressure actually acting on carbon atoms well follows the setting pressure of the Andersen barostat method. In this simulation, we could demonstrate the transition from graphite to diamond at the pressure of 15 GPa, which is in agreement with an experimental report, as shown in Fig. 2. The quantitative representation of the transition from graphite to diamond was given by the change in the ratios of the numbers of sp^2 and sp^3 carbon atoms to that of all carbon atoms as in Fig. 3, which are here called sp^2 and sp^3 ratios, respectively. As the pressure increased, the sp^2 ratio decreased and the sp^3 ratio increased. When the pressure reached 15 GPa, the sp^3 ratio also became 1.0. That is, carbon atoms became a perfect sp^3 material. From the simulation snapshot shown in Fig. 2 (last), it was confirmed that when the sp^3 ratio was 1.0, the carbon atoms formed a diamond structure, not an amorphous structure.

### Table I. Compositions of deposits.

| Optimized parameter | Optimal value | Fixed parameter | Fixed value |
|---------------------|---------------|-----------------|-------------|
| Q                   | 3.867623      | r_m (Å)         | 1.7         |
| K_m (eV)            | 0.946244      | r_u (Å)         | 0.5         |
| a_m (Å)             | 1.106056      | q^0             | 4           |
| K_m (eV)            | 1.343592      |                  |             |
| a_m (Å)             | 0.652446      |                  |             |
| K_m (eV)            | 0.229646      |                  |             |
| a_m (Å)             | 0.951189      |                  |             |
| K_m (eV)            | 0.712260      |                  |             |
| a_m (Å)             | 1.144283      |                  |             |
| K_m (eV)            | 0.790185      |                  |             |
| a_m (Å)             | 0.439343      |                  |             |
| K_m (eV)            | 1.007662      |                  |             |
| a_m (Å)             | 1.058837      |                  |             |
| K_m (eV)            | 1.307662      |                  |             |
| a_m (Å)             | 1.078244      |                  |             |

#### 3.2 Deposition of amorphous carbon

Using the present new potential model, we tried to simulate the deposition generating an sp^3-rich amorphous carbon. The manner of the MD simulation of deposition was similar to that in our previous work. The substrate was an sp^3-rich amorphous carbon material prepared by the MD simulation of deposition using the REBO2002 potential. The sp^3 ratio of the substrate was about 20%. The size of the surface of the substrate was 2.019 × 2.186 nm^2, and the substrate was put on the simulation box, which was under the periodic boundary condition in the direction parallel to the surface of the substrate. The carbon atoms initially put on the simulation box as the substrate were connected to the Langevin thermostat with a friction coefficient of 1.0 × 10^{14} s^{-1} to control the temperature, where the motion of carbon atoms located in the range of up to 0.12 nm from the bottom position was fixed during simulation. In one simulation, 1000 carbon atoms as a source were continuously injected from 3.4 nm above the initial surface of the substrate every 1.0 × 10^{13} s. The injection position parallel to the surface of the substrate was determined randomly under a uniform distribution. These MD simulations were executed by varying the injection energy from 1 to 200 eV.

As a result of the MD simulation using the present new potential, we could obtain the sp^3-rich amorphous carbons as deposits. Figure 4 shows the sp^3 and sp^3 ratios of carbon atoms in the deposit, except for the substrate. From this figure, it was confirmed that the sp^3 ratio in the case of the present new potential was greater than that in the case of the REBO2002 potential for all the injection energies considered.

The penetration depth of the injected carbon atoms was also investigated, as shown in Fig. 5. Here, the penetration depth was defined as the average distance between the surface position at the moment of each injection and the final position of each injected carbon atom. In the case using the present new potential, the penetration depth increased as the injection energy increased higher than 20 eV, while it was independent of the injection energy for a lower range. On the
other hand, in the case using the REBO2002 potential, the injected carbon atoms hardly penetrated the surface. The penetration depth in the case of the injection energy of 200 eV corresponds to three times the thickness of diamond and graphite monolayers.

The deposition rate was also estimated by the time evolution of the thickness of the deposit, as shown in Fig. 6. Here, the thickness was defined by the difference in the surface position where the minimum position during

---

**Fig. 2.** (Color online) Animation snapshots in the MD simulation for transition from graphite to diamond at a pressure of 15 GPa. The green and red spheres indicate sp\(^2\) and sp\(^3\) carbon atoms, respectively. The white lines show the side of the simulation box under the periodic boundary condition.

**Fig. 3.** Sp\(^2\) and sp\(^3\) ratios, which are defined as the ratios of the numbers of sp\(^2\) and sp\(^3\) carbon atoms to that of all carbon atoms, as functions of elapsed time.

**Fig. 4.** Sp\(^2\) and sp\(^3\) ratios of injected carbon atoms in deposits. The white and black rectangles indicate sp\(^2\) and sp\(^3\) ratios evaluated by MD simulation with the present new potential, respectively. The white and black spheres indicate those with the REBO2002 potential, respectively.

**Fig. 5.** Penetration depth of carbon atoms as a function of injection energy. The penetration depth is the mean of that for all injected carbon atoms except for sputtered ones. The circular and square points indicate the calculated depths by using the REBO2002 and new potentials, respectively.

---

200 eV corresponds to three times the thickness of diamond and graphite monolayers.

The deposition rate was also estimated by the time evolution of the thickness of the deposit, as shown in Fig. 6. Here, the thickness was defined by the difference in the surface position where the minimum position during
simulation was set to zero. The thickness decreased for a while from the start of simulation because of the contraction of the substrate. The substrate, composed of stacked amorphous blocks, which was created by using the REBO2002 potential, had an sp^3-rich structure, which is an unstable state for the present new potential, and the thickness decreases. The simulation in the case of high-energy injection used many amorphous blocks to prepare the substrate, and the decrease in thickness was larger. After the contraction of the substrate, the thickness increased linearly. By this linear growth, the deposition rate could be evaluated as the gradient of the increase in thickness. It is understood that the deposition rate was independent of the injection energy of less than 100 eV because sputtering hardly occurred. In the case of an incident energy of 100 eV or more, we should calculate a longer time.

4. Discussion

In the present paper, we proposed a new potential model. In fact, before developing the new potential model, we had tackled the modification of the REBO2002 potential to represent the sp^3-rich amorphous carbon. In particular, in terms of the three body terms depending on bond angles, many function forms were tried and parameters were optimized by using the downfolding method every time. However, we could not obtain a well-modified potential to achieve the transition from graphite to diamond owing to high pressures. Compromising the optimization of parameters, graphite kept its structure even at a pressure of over 100 GPa or it changed to highly oriented structures. From this experience, we consider that an approximation of the interaction of a covalent bonding system with the bond angle, dihedral angle, and so on, which are historically employed by BO-type potential models, does not give us a good representation for amorphous structures, which are metastable. For a stable structure, it was reported that the elastic constant of diamond is not properly evaluated by the REBO potential.20)

On the basis of the above discussion, the bond and dihedral angles were not employed as the variables of the function form of the present new potential. In the new potential, the electron distribution was considered as a point charge, and the potential function consists of nuclear–nuclear repulsion, nuclear–electron attraction, and electron–electron repulsion as the functions of only distance between atoms.

Our idea, which is the point charge simplifying the electron distribution, is analogous to the bond charge model (BCM) proposed by Weber.21) The BCM was developed to represent the diamond structures of C, Si, Ge, and Sn. In the BCM also, the point charge was put at the center of a covalent bond, where it is called the “bond charge”. Although there are differences between the present new model and the BCM in function forms, the present new potential corresponds to an extended model of the BCM. The two greatest differences are that the point charge on a covalent bond is a variable function of a distance between atoms to enable the connection and disconnection of the covalent bond and that all function forms are composed of only distances between atomic pairs without the bond and dihedral angles by the above experience. Consequently, we could easily achieve the transition from graphite to diamond at high pressures. We carried out the downfolding for this function form, and we could smoothly optimize all parameters.

Here, we compare the present new potential with two representative potential models for carbon systems, Brenner’s REBO2002 potential and the Tersoff potential.22) Figure 7 shows the potential energy of the new potential model during the actual MD simulation of the transition from graphite to diamond in Sect. 3.1, and the potential energies calculated by REBO2002 and Tersoff potentials, and DFT in terms of 77 types of atomic geometry replicated from the MD simulation every 0.04 ps. The potential energies obtained by the new potential are close to those obtained by DFT, while those obtained by the REBO2002 potential are significantly different from those obtained by DFT. This comparison implies the advantage of the present new potential over the REBO2002 and Tersoff potentials in terms of amorphous carbon structures. Intriguingly, the Tersoff potential seems to be better for amorphous carbon structures than the REBO2002 potential.

Furthermore, the present transition pressure of 15 GPa agreed with an experimental report.23) Almost all MD simulations of the transition of graphite to diamond at comparable pressures to the experiment by the other researchers employed the quantum chemical theory to calculate the energy and force of atoms.24–30) It is interesting to reflect that the present new potential is classified into the category of classical mechanics, even though it can demonstrate the transition of graphite to diamond at a proper pressure.

5. Conclusions

In the present work, we were aware that the reason why sp^3-rich amorphous carbon materials are not well generated by MD simulation is that the REBO2002 potential, which is a major model, cannot give a correct interaction energy in terms of amorphous carbon structures. To solve this problem, we developed a new potential, which was modeled according to the natural consideration that the interaction
among atoms consists of attraction and repulsion between nuclei and electrons. Then, the electron distribution was simplified as a point charge located around atoms. Consequently, using the present new potential, we could generate sp\(^3\)-rich amorphous carbon deposits. In addition, we could demonstrate the transition from graphite to diamond at a pressure of 15 GPa, which corresponded to an experimental report.\(^7\)

To advance the research for amorphous carbon deposition, the treatment of hydrogen atoms is necessary. As an additive substance, catalyst or impurity, more atomic elements are needed. Therefore, we should aim to extend the potential model. To treat many other atomic geometries and elements, the improvement in the representation of a point charge toward /C\(^2\)\(_5\)-electrons and unshared electron pairs is considered. To achieve better agreement in potential energy, reoptimization by the downfolding method into the reference energy calculated by higher level quantum chemical calculation methods is effective.

Acknowledgments

We are very grateful to Dr. Y. Yoshimoto for useful discussion and comments on the downfolding method, and to Professor N. Ohno and Mr. N. Hirata for helpful comments on amorphous carbon deposition. We would also like to thank Professor T. Ozaki for offering “OpenMX” and Dr. M. Nishio for helpful comments related to how to use it. Numerical simulations were carried out by using the Plasma Simulator at the National Institute for Fusion Science. The present work was supported by Grants-in-Aid for Scientific Research (Nos. 19055005 and 23710135) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, NINS Program for Cross-Disciplinary Study, and NIFS Collaboration Research program (NIFS09KNSS002 and NIFS11KNTS008).

References

1) W. Jacob and W. Moller: Appl. Phys. Lett. 63 (1993) 1771.
2) J. Robertson: Mater. Sci. Eng. R 37 (2002) 129.
3) S. Saito, A. M. Ito, A. Takayama, and H. Nakamura: Jpn. J. Appl. Phys. 51 (2012) 01AC05.
4) D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott: J. Phys.: Condens. Matter 14 (2002) 783.
5) A. Ito, H. Nakamura, and A. Takayama: J. Phys. Soc. Jpn. 77 (2008) 114602.
6) A. M. Ito, A. Takayama, S. Saito, N. Ohno, S. Kajita, and H. Nakamura: Jpn. J. Appl. Phys. 50 (2011) 01AB01.
7) F. P. Bundy and J. S. Kasper: J. Chem. Phys. 46 (1967) 3437.
8) D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott: J. Phys.: Condens. Matter 14 (2002) 783.
9) Y. Yoshimoto: J. Chem. Phys. 125 (2006) 184103.
10) OpenMX web-site: http://www.openmx-square.org/
11) P. Hohenberg and W. Kohn: Phys. Rev. 136 (1964) B864.
12) W. Kohn and L. J. Sham: Phys. Rev. 140 (1965) A1133.
13) J. P. Perdew, K. Burke, and M. Ernzerhof: Phys. Rev. Lett. 77 (1996) 3865.
14) T. Ozaki: Phys. Rev. B 67 (2003) 155108.
15) T. Ozaki and H. Kino: Phys. Rev. B 69 (2004) 195113.
16) N. Troullier and J. L. Martin: Phys. Rev. B 43 (1991) 1993.
17) T. Ozaki and H. Kino: Phys. Rev. B 72 (2005) 045121.
18) H. C. Andersen: J. Chem. Phys. 72 (1980) 2384.
19) G. Gao, K. V. Workum, J. D. Schall, and J. A. Harrison: J. Phys.: Condens. Matter 18 (2006) S1737.
20) W. Weber: Phys. Rev. B 15 (1977) 4789.
21) J. Tersoff: Phys. Rev. B 39 (1989) 5566 [Erratum 41 (1990) 3248].
22) C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho: J. Phys.: Condens. Matter 4 (1992) 6047.
23) S. Scandolo, M. Bernasconi, G. L. Chiarotti, P. Focher, and E. Tosatti: Phys. Rev. Lett. 74 (1995) 4015.
24) Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki: Phys. Rev. B 54 (1996) 14994.
25) A. De Vita, G. Galli, A. Canning, and R. Car: Nature 379 (1996) 523.
26) A. De Vita, G. Galli, A. Canning, and R. Car: Appl. Surf. Sci. 104–105 (1996) 297.
27) X. Wang, S. Scandolo, and R. Car: Phys. Rev. Lett. 95 (2005) 185701.
28) G. Kern and J. Hafner: Phys. Rev. B 58 (1998) 13167.
29) F. Zipoli, M. Bernasconi, and R. Martonák: Eur. Phys. J. B 39 (2004) 41.
30) Y. Omata, Y. Yamagami, K. Tadano, T. Miyake, and S. Saito: Physica E 29 (2005) 454.