The First principle calculation of bulk modulus and Young's modulus for amorphous carbon material

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Abstract. The dependence of bulk modulus and Young's modulus on mass density for hydrogen-free amorphous carbon structures were investigated by using the first principle calculation on density functional theory. The amorphous carbon structures with various mass densities were generated by the numerical operations of structure relaxation from the random structures and volume relaxation. The bulk modulus and Young's modulus increased in proportion to the mass density. We uses the number densities of sp\(^3\) and sp\(^2\) atoms in place of these fractions or ratios as a classification parameter of amorphous carbon material because the number density of sp\(^3\) atoms can fit the both of amorphous carbon and diamond by one straight line in bulk modulus and Young's modulus. By this analysis, we suggest that the increases of the bulk modulus and Young's modulus are derived from only the sp\(^3\) carbon atom.

1. Introduction
Amorphous carbon materials include the various kinds of properties depending on the methods of fabrication. A part of them is elastic modulus and hardness close to those of a diamond. The hard amorphous carbon materials are called diamond like carbon (DLC), and then the DLC is used for industrial purposes such as coating. It is considered that the higher elastic modulus and hardness of amorphous carbon material is derived from the tetrahedral structure of sp\(^3\) bonding of carbon atoms. Therefore, hard amorphous carbon is usually classified into tetrahedral amorphous carbon (ta-C). The relation between the elastic modulus and the sp\(^3\) fraction, which is the ratio of number density of sp\(^3\) carbon atoms to the number density of all kinds of carbon atoms, is often regarded as one of the most important features for the classification of amorphous carbon materials [1-6]. For example, the dependence of Young's modulus and hardness on sp\(^3\)/sp\(^2\) ratio [7,8] was researched. In addition, because the ta-C has higher mass density close to that of a diamond, mass density is also used for the classification of amorphous carbon material. The dependence of sp\(^3\) fraction [9,10], the Young's modulus [5,11-13] and shear modulus [12] on mass density were researched.

However, the factor to complicate the classification of amorphous carbon material is the containing of hydrogen atoms. Hydrogen atoms eliminate dangling bond, and but carbon atoms terminated by hydrogen atoms cannot construct tetrahedral carbon network structure. Namely, elastic modulus and hardness decrease as hydrogen content increases. Actually, for almost all of hydrogenated amorphous carbon, Young's modules is 250 GPa or less [7,8]. On the other hand, that Young's modulus of...
hydrogen free amorphous carbon which is created by using mass-selected ion beam (MSIB) deposition is 680 GPa [4].

Theoretical study on amorphous carbon material is fewer than experimental researches. Theoretical approach is necessary to solve the classification of amorphous carbon material. Especially, numerical simulation in virtual environments can simplify the complex feature of amorphous carbon material. Deposition process is often simulated by using molecular dynamics (MD) simulation [14,15]. We had also investigated the dependence of deposition rate on dependence on H/C ratio by using MD [16]. Moreover, amorphization from graphite due to hydrogen plasma irradiation was investigated with the hybrid simulation of MD and binary collision approximation (BCA) [17]. However, the problem in the MD and MD-BCA hybrid simulations is that the simulation result strongly depends on the accuracy of interatomic potential model. Especially, physical properties evaluated from MD are unreliable in amorphous carbon materials [15].

Although we had improved the quality of potential model for carbon system [18], the first principle calculation based on the density functional theory (DFT) is more suited to the evaluation of physical properties.

In this paper, we challenge to clarify mass density and \( \text{sp}^3 \) fraction dependences of bulk modulus and Young's modulus in amorphous carbon material, where we only treat hydrogen free amorphous carbon material to simplify the problem. In order to evaluate correct value of bulk modulus and Young's modulus, fully DFT calculation is employed in the present research. Simulation method and code for DFT calculation are introduced in section 2. Amorphous carbon material was created by numerical approach in section 2.2. In section 3, Bulk modulus and Young's modulus of the amorphous carbon material are calculated and then we discuss about dependence on mass density and \( \text{sp}^3 \) fraction. This paper ends with conclusions in section 4.

2. Simulation method

2.1. Density functional theory

In the present paper, the first principle calculation of the total energy and forces are executed based on the density functional theory (DFT). In the DFT, the wave function for the electrons bound by atomic nuclei is solved on the Kohn-Sham equation [19,20]. The total energy as a solution of the Kohn-Sham equation for amorphous carbon structures was calculated with Open source package for Material eXplorer (OpenMX) [21] code, which is numerical simulation software based on DFT.

The generalized gradient approximation (GGA) with a Perdew-Burke-Ernzerhof (PBE) functional [22] was employed as an exchange-correlation potential. Only the valence electrons were explicitly simulated by using norm-conserving pseudo-potentials [23]. The wave functions were numerically represented by linear combinations of pseudo-atomic orbitals (LCPAOs) [24,25]. The cutoff energy was set to 250 Rydberg.

2.2. Creation of amorphous carbon geometry

Amorphous carbon structures were prepared in numerical simulation. To put it briefly, we find the structure in which force acting on each atoms calculated by DFT balances.

Cubic simulation box of size 1.0 nm on a side with the periodic boundary condition is set. Carbon atoms are put into the simulation box at random positions. The forces acting on atoms are calculated by DFT from the current structure, and then the atoms are moved by minute distances along the directions of the forces. By iterating these operations, the structure at which all force balances is obtained. This method is, in general, called structure relaxation. In the present paper, to reduce the number of iteration, the amounts of movement of atoms are determined by using the Broyden-Fletcher-Goldfarb-Shanno method [26-29], which is one of quasi Newton methods. The iteration was finished when the maximum magnitude of the force vector is smaller than \( 3.0 \times 10^{-4} \) hartree/bohr. The ten kinds of amorphous structure are prepared varying the number of carbon atoms from 80 to 175, which are corresponding to the mass density from 1.59g/cc to 3.49g/cc.
Figure 1. The structure relaxation from the left structure to the right structure. The color of atoms indicate the coordination numbers of atoms. The yellow, green and red spheres indicate sp$^1$, sp$^2$ and sp$^3$ atoms, respectively. The blue and purple spheres indicate lower and higher coordination atoms.

Figure 1 shows the structure change before and after the structure relaxation. From this figure, it is confirmed that all of carbon atoms which have higher or lower coordination numbers changes into the carbon atoms which have the coordination numbers from two to four.

The validation of the amorphous structure created by the above structure relaxation was to check the radial distribution function. All of the amorphous structures created in the present work have the radial distribution function like a liquid state.

By the above operation of structure relaxation, the forces acting on atoms balance, i.e. forces becomes zero. However, stress is applied to the whole of system since the fixed volume of simulation box under the periodic boundary condition. In some cases, the amorphous structures are narrowly kept by the bound by the fixed size of simulation box. Therefore, we should relax the amorphous structures by varying the volume of the simulation box, which is called volume relaxation here.

In the operation of the volume relaxation, the size of simulation and atomic positions are isotropically scaled. The atomic position after structure relaxation $\mathbf{r}$ and the side of initial simulation box $L$ is scaled with the scaling factor $s$.Scaled atomic position becomes $\mathbf{r}' = s\mathbf{r}$ and the scaled side of initial simulation box becomes $sL$. The total energy $U(\mathbf{r}')$ is function of the scaling parameter $s$ via the scaled atomic position. By iterative calculation of total energy varying $s$, we obtained the solution $s_0$ of an equation $\partial U(s\mathbf{r})/\partial s = 0$. As a result, atomic position and the side of simulation box after these volume relaxation are $\mathbf{r}'_0 = s_0\mathbf{r}$ and $L'_0 = s_0 L$, respectively. Since the volume of the simulation box was changed, the mass densities of the amorphous carbon structures after volume relaxation becomes 1.64 g/cc to 3.06 g/cc.

Note that isotropic stress is reduced by the volume relaxation. The derivative of total energy $\partial U(s\mathbf{r})/\partial s$ by the scaling factor $s$ can be given by

$$\frac{\partial U(s\mathbf{r})}{\partial s} = -\frac{1}{s} \sum_{i} F_i \cdot \mathbf{r}'_i$$

(1)

where $\mathbf{r}'_i$ is the position of $i$-th atom and the force acting on the $i$-th atom $F_i = -\partial U(\mathbf{r}')/\partial \mathbf{r}'_i$. The right hand term in equation (1) corresponds to isotropic stress in the particle picture [30]. When the derivative of total energy $\partial U(s\mathbf{r}_0)/\partial s = 0$, then the isotropic stress becomes zero.
2.3. Calculation of Bulk modulus and Young’s modulus

For the ten kinds of amorphous structures by the above operations of structure relaxation and volume relaxation, Bulk modulus and Young’s modules are evaluated by using the DFT calculation.

Bulk modulus can be calculated by the isotropic scaling operation same to the volume relaxation. Here, we redefine atomic positions and simulation box after the above volume relaxation as \( r \) and \( L_0 \). They are re-scaled by the scaling factor \( s \), and then the bulk modulus is given by

\[
K = \frac{1}{9L_0^3} \left[ -\frac{2}{s^2} \frac{\partial U(sr)}{\partial s} + \frac{1}{s} \frac{\partial^2 U(sr)}{\partial s^2} \right]
\]  

(2)

In actual operation, the bulk modulus is obtained from same calculation to the volume relaxation.

Young’s modulus is calculated by one dimensional scaling operation. In the present paper, we performed only the scaling in the \( x \) direction with the scaling factor \( s_x \). The atomic positions are changed from \( r = (x, y, z) \) to \( r' = (s_x x, y, z) \) and the side of the simulation box in \( x \) direction is changed from \( L_{0,x} \) to \( s_x L_{0,x} \). The Young’s modulus is given by

\[
E = \frac{1}{L_0^3} \frac{\partial^2 U(r'')}{\partial s_x^2}
\]  

(3)

3. Results and discussion

By the operations of the structure relaxation and volume relaxation in section 2, the ten kinds of amorphous carbon structure, which has difference in mass density. The mass density of these amorphous structures are for the range from 1.64 g/cc to 3.06 g/cc.

Figure 2 shows the bulk modulus of amorphous carbon material as a function of mass density. The bulk modulus increases in proportion to the mass density. This proportionality coefficient is estimated as 133.9 GPa·cc/g. In addition, we calculated the bulk modulus of a perfect crystalline diamond. The evaluated value of bulk modulus of the perfect crystalline diamond by DFT was 450.6 GPa. The bulk modulus of the perfect crystalline diamond can be placed on the approximate straight line which generated by fitting the bulk modulus of amorphous carbon proportional to the mass density.

Figure 3 shows the Young’s modulus of amorphous carbon material as a function of mass density. As well as the bulk modulus, the Young’s modulus increases in proportion to the mass density. This proportionality coefficient is estimated as 434.3 GPa·cc/g. The Young’s modulus of the perfect crystalline diamond was evaluated as 1116.2 GPa by DFT. The Young’s modulus of the perfect crystalline diamond is also placed on the approximate straight line generated by fitting the bulk modulus of amorphous carbon material.
modulus of amorphous carbon proportional to the mass density.

The proportionality of the Young's modulus and mass density was also reported by experiment [5]. The proportionality coefficient estimated from experimental reported data is about 530 GPa·cc/g and it is agreement with our calculation results. We consider that the difference in the proportionality coefficient between the present calculation and experimental report is caused by the variability among sample structures of amorphous carbon in this calculation. Especially, for the small range of mass density, the amorphous structures include larger void spaces. The variety of the position and configuration of the large void spaces causes the variability of mechanical property.

To explain the dependences of the bulk modulus and the Young's modulus on mass density, we counted the covalent bonds of amorphous carbon materials. Figure 4 shows the number density of covalent bonds, which is the number of covalent bonds per unit volume, as a function of mass density. It is found that the number density of covalent bonds increases in proportion to mass density as well as the bulk modulus and Young's modulus. This fact implies that the bulk modulus and Young's modulus is simply proportion to the number of covalent bonds.

Further, sp$^1$, sp$^2$ and sp$^3$ atoms were counted in amorphous carbon materials, where the classification of carbon atoms into sp$^1$, sp$^2$ and sp$^3$ states is simply according to coordination number. Figure 5(a) shows sp$^1$, sp$^2$ and sp$^3$ fractions as functions of mass density. It is found that the sp$^3$ fraction increases in proportion to mass density. The present calculation result well agrees with the experimental measurement [9,10] on the fact that the linear increase of sp$^3$ fraction from 0.2 at 2.2 g/cc to 0.8 at 3.0 g/cc.

However, the sp$^3$ fraction of the perfect crystalline diamond, which is 1.0, is not located on the approximate straight line of linear proportionality in figure 5(a). Therefore, we recommend the use of the number density of sp$^3$ carbon atom, which is the number of sp$^3$ carbon atoms per unit volume, in place of the sp$^3$ fraction. Figure 5(b) shows the number densities of sp$^1$, sp$^2$ and sp$^3$ atoms as functions of mass density. In the representation by the number densities of sp$^3$ atoms, the value of the perfect crystalline diamond is located on the approximation straight line of linear proportionality.

The representation by number density is superior in terms of sp$^2$ carbon atoms also. In the representation by fraction in figure 5(a), the sp$^2$ fraction decreases as mass density increases, while in the representation by number density in figure 5(b), the number density of sp$^2$ hardly changes for the range of 2.8 g/cc or less. This fact implies that the decrease of sp$^2$ fraction is apparent decrease associated with by the increase of sp$^3$ atoms.

Thus, the total number density of covalent bonds and the number density of sp$^3$ atoms increase in proportion to mass density. This fact implies that the increases of the bulk modulus and Young’s modulus are brought about the increase of sp$^3$ carbon atoms or simply covalent bonds. The bulk modulus and Young’s modulus hardly had correlation with the number density of the sp$^2$ carbon atoms.
Finally, we note the problem to advance the present analysis with the above numerical simulation. One problem is the variability among sample structures of amorphous carbon. Especially, the amorphous carbon has the small mass density, which has sp\(^2\) rich structure, easily create larger void spaces. In order to more accurate evaluation of elastic modulus, the calculation of many sample structures is required. The other problem is that the space scale in the present simulation is small. If the size of sample amorphous structures are enough large, the variability among the sample structures becomes vanishingly small. Moreover, the real large scale amorphous carbon material, which means the material treated in real experiment, has certainly precipitated crystalline grains and long range order structure. These are effective to the mechanical property such has elastic modulus. To treat the precipitated crystalline grains and the long range order structure, at least sub-micro meter scale is required. Classical MD simulation can be used for the evaluation of mechanical property of the large scale amorphous structures, where the interaction potential model for classical MD should be improved to represent the realistic amorphous carbon material \[18\].

4. Conclusions

In this paper, we investigated the bulk modulus and Young's modulus of hydrogen-free amorphous carbon structures by using the first principle calculation on density functional theory. The amorphous carbon structures which have various mass densities for the range from 1.64 g/cc to 3.06 g/cc were reproduced by the operations of the structure relaxation from the random structures and the volume relaxation. For the reproduced amorphous, we showed that the bulk modulus and Young's modulus increases in proportion to the mass density. The number density of sp\(^3\) carbon atoms in amorphous carbons also increases in proportion to the mass density, while that of sp\(^2\) carbon atoms does not increase with the mass density. From this fact, we suggest that the increases of bulk modulus and Young's modulus in hydrogen-free amorphous carbon materials are produced by the increase of the sp\(^3\) carbon atoms or the increase of covalent bonds simply.

As a new classification parameter, we proposed the number densities of sp\(^2\) and sp\(^3\) atoms in place of these fractions. The superiority of the representation by number density is evident from the two facts that the number density of sp\(^3\) atoms can fit amorphous carbon and the perfect crystalline diamond by one straight line and that the remaining of the number density of sp\(^1\) was shown. The number densities of sp\(^2\) and sp\(^3\) are obtained by simple transformation from the sp\(^3\) and sp\(^2\) fractions.

In future work, hydrogenated amorphous carbon will be analysed by similar method with DFT calculations. Not only elastic modulus, electronic property of amorphous carbon can be investigated by DFT. However, much more sample structures should be prepared to vanish the variability among the sample structures of amorphous carbon, especially for the range of small mass density. In association with this problem, the existence of the amorphous structures which have same sp\(^3\)/sp\(^2\) ratio and but differs in bond orientation due to the difference of fabrication method was predicted \[31\]. MD
is necessary for the simulation of various fabrication of amorphous carbon and the simulation of larger amorphous structure including the precipitated crystalline grains and the long range order structure. Therefore, we should use both MD and DFT simulations as the situation demands.

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