

First-principles Molecular Dynamics Simulations for the Properties of Boron-doped Tetrahedral Amorphous Carbon

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Abstract

Based on first-principles molecular dynamics (FPMD) simulations combined with a liquid quenching method, we study the effects of boron doping at 0%, 2%, 4%, 6% on the properties of tetrahedral amorphous carbon (ta-C) with an initial density of 3.0 g/cm³. The results of bond structures and internal stress show the promotion of graphitization with increase in the concentration of boron doping. In addition, simulation of electronic states reveals that the Fermi level shifts to valence band and the intensity of density of electronic states near Fermi level increases with the boron concentration increasing. A covalent bond formation between carbon and boron atoms is also shown by analyzing projected densities of electronic states (PDOS) and electron density distribution. The results of electronic state and bond formation strongly indicate that the boron-doped ta-C is like a p-type conductor. The present simulation results provide useful information for deeper understanding on the physical properties of boron-doped ta-C.

- 1 Keywords: Boron-doped amorphous carbon; First-principles molecular dynamics; Liquid
- 2 quenching method
- 3

1. Introduction

As a specific type of amorphous carbon, tetrahedral amorphous carbon (ta-C) has a high sp^3 content over 60% with no hydrogen element in the structure [1]. Ta-C films have an excellent electrochemical stability [2] and wear resistance [3], and can be used as protective coatings in industrial fields [4]. The films of ta-C are prepared using many deposition techniques, such as filtered cathodic vacuum arc (FCVA), magnetron sputtering, and laser ablation [5-7]. The maxima of density, Young's modulus and internal stress of ta-C are achieved by pulse arc discharge plasma method at ions energy of 50-70 eV [8]. It is also shown that the Young's modulus and density of ta-C depend on the sp^3 fraction strongly [9].

The properties of ta-C can be modified by dopant [10-13]. Boron is often used as a doping element in the ta-C films. Experimentally, Tan *et al.* [14] prepared boron-incorporated ta-C (ta-C:B) films with concentration from 0% to 6.04 at.% by FCVA deposition, and found that a clustering of sp^2 sites appears in the ta-C films without obvious decrease in content of fourfold coordinated carbon atoms. In contrast, several studies reported that boron-doped ta-C films become richer in fraction of sp^2 hybridized carbon when the boron doping level increases [15-17]. Chhowalla [18] achieved boron doping in ta-C films with boron content of 2% and 4% using FCVA method, and found that internal stress can be reduced to 1-3 GPa without the sp^3 content decreasing, while the resistivity increases by two orders of magnitude after boron doping. Kleinsorge [19] found that the room temperature conductivity of boron-doped ta-C films deposited by FCVA increases by five orders of magnitude after doping content is up to 8%, and the sp^2 fraction is nearly constant within boron concentration below 4%. Panwar [20] deposited ta-C films with boron content up to 2.0 at.% using FCVA method. They found that

boron doping brings about nearly an order increase in conductivity and sp^3 content decreases from 92.0% to 88.4%.

As shown above, different experimental studies bring about different results about the effects of boron doping on the properties of ta-C. Theoretical study, irrespective of thin film growth techniques, is a good way to investigate the doping effects under ideal conditions. Gambirasio and Bernasconi [21] performed an *ab initio* dynamical simulation of boron doping in 64-atoms ta-C systems with boron contents of 1.6% and 3.2% in box of constant volume. Their study indicated that boron is mainly in sp^2 hybridization states and the boron doping does not have the effect on the fraction of sp^3 hybridized carbon atoms. Park *et al.* [22] investigated energetics, structure, and electronic and mechanical properties of the B doped amorphous carbon films with density of 2.9 g/cm³ using first-principles calculation. A very slow cooling rate of -250 K/ps was used in their study and the results about effects of boron doping on sp^3 contents and energy bands were not provided. However, few theoretical studies of the effects of boron doping on the physical properties in ta-C have been conducted so far. In this study, making use of first-principles molecular dynamics (FPMD) simulations, we investigate the effects of boron doping of low content (0-6%) on the properties of ta-C using liquid quenching method, such as hybridization states of atoms, internal stress and bond feature.

2. Computational methods

200 carbon atoms were distributed randomly in a cubic box with a side length of 11 Å, which corresponds to an initial density of 3.0 g/cm³. Boron doping with contents of 2%, 3%, 4%, and 6% was accomplished by substituting carbon atoms existing in the pure carbon system. It was

1 worth noting that there were almost negligible changes of density even at the maximum boron
 2 doping (6%), with density decreasing from 2.99 g/cm³ to 2.98 g/cm³. The present system with
 3 200 carbon atoms is the largest in the simulations on boron-doped ta-C till now, which can
 4 better represent the realistic properties of systems. Furthermore, boron doping range in our
 5 simulation is wider compared to the previous simulation studies. The gaussian and plane-wave
 6 (GPW) method, implemented in CP2K code [23] was used to do calculations. Open source
 7 program OVITO [24] was used to do data processing and visualization. All the calculations
 8 adopted canonical (NVT) ensemble and used periodic boundary conditions in XYZ directions
 9 of simulation box. Lennard-Jones thermostat [25] was used to control the temperature with the time
 10 step set to 1 fs. Since boron doping may generate unpaired electrons in these systems, spin-
 11 polarized calculations were performed here [26]. Due to the relatively large number of particles
 12 in the system, the Γ point only is enough to sampling Brillouin zone. Five multigrids were
 13 adopted and the charge density cutoff for the finest level of multi-grid was set as 400 Ry [27].
 14 The basis set of QZVP-MOLOPT-SR-GTH [28] and pseudopotential of Goedecker-Teter-
 15 Hutter [29,30] were used for carbon and boron atoms. The Perdew-Burke-Ernzerhof (PBE)
 16 functional [31] was elected to represent the exchange-correlation term of Kohn-Sham equations
 17 [32]. Liquid quenching method was taken into account in order to obtain all the ta-C structures,
 18 which emulates the process of heat dissipation of thermal spike. The previous study indicated
 19 that the lifetime of thermal spike was approximately 0.1 ps, which corresponds to quenching
 20 from 5000 K to 3000 K [33]. McCulloch [34] obtained amorphous carbons at densities of 2.0-
 21 3.2 g/cm³ by using liquid quenching method along a temperature curve of the form $T=5000e^{-ct}$
 22 (T : temperature, t : time) in 0.5 ps from 5000 K to 300 K (0.09 ps was spent corresponding to

temperature cooling from 5000 K to 3000 K), and their amorphous structure with a density of 2.9 g/cm³ was in good agreement with experimental neutron diffraction data. In our calculations, we used the same exponential cooling method as McCulloch did, but the time spans for quenching from 5000 K to 3000 K were kept at 0.1 ps basically by adjusting variation curves of temperature.

One might think that since the surface of film is exposed to atmosphere the NPT ensemble is more appropriate. However, when NPT ensemble is used, temperature can't be controlled well and the quenching process is not easily achieved. To our best knowledge, no study has been reported to date that quenching process is performed using NPT ensemble in this area. On the other hand, when NVT ensemble is used, we can control system temperature well and the quenching process can be performed properly. NVT ensemble is utilized also in previous studies to emulate the thermal spike during ta-C growth [21,22,34]. Our study is based on the previous studies.

The simulation process was described using the standard case in simulation of the system with doping content of 2% as follows: (1) The target temperature was set at 5000 K to produce liquid-state structure. Because of the energetic instability of the initial structure, the system melted instantly and the temperature increased to nearly 17000 K, then gradually decreased to the target temperature 5000 K during 1.5 ps. (2) The system was kept at 5000 K for another 0.5 ps to ensure sufficient diffusion of particles and eliminate the influence of the initial structure. (3) The liquid system was cooled rapidly to temperature near 300 K along a temperature curve of form of $T=5000e^{-ct}$ (the value of c is approximately 0.0052) in 0.5 ps. (4) Conjugate gradient algorithm was used to perform structural optimization to obtain the final structure. Atomic

relaxation was repeated until the force acting on each atom was less than 0.01 eV/Å. The temperature versus time changing and the obtained final structure corresponding to the system with doping content of 2% are shown in Fig. 1 and Fig. 2, respectively.

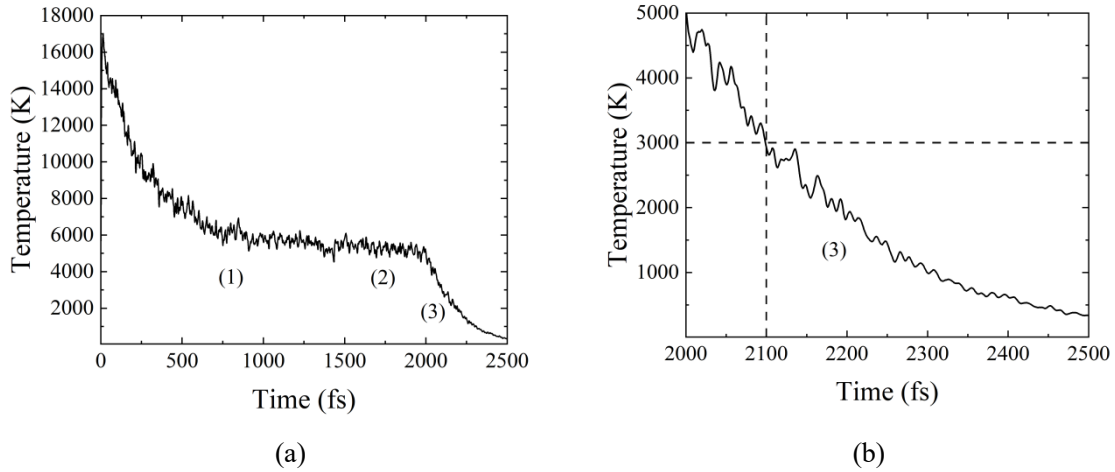


Fig.1. (a) Temperature profile as a function of simulation time in the whole simulation. (b) The temperature variation curve during the quenching stage (stage (3)) in Fig.1(a) is enlarged, where the dashed lines show the quenching time of 0.1 ps corresponding to the time span for quenching from 5000 K to 3000 K. The numbers (1), (2), and (3) represent different simulation process described in the text.

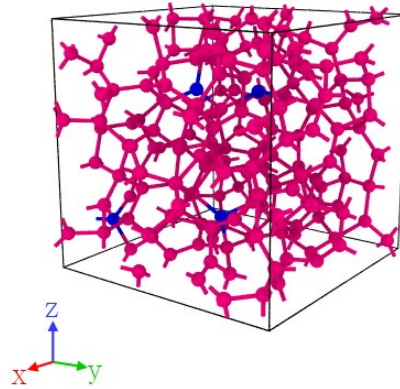


Fig.2. Final structure after structural optimization. Red and blue balls represent carbon and boron atoms, respectively. The cutoff distance of 1.85 Å is used to determine the existence of chemical bonds.

3. Results and discussion

3.1 Coordination number and stress

Effects of the boron doping on coordination number of carbon atoms in the ta-C are investigated in this study. Experimentally, the fraction of sp^3 carbon is determined by the spectral analysis of X-ray photoemission spectroscopy. That is, the C1s peak in ta-C is decomposed into several components, and the sp^3 fraction is determined by the ratio of sp^3 peak area. In order to compare with experimental results, only the variations of sp^3 content corresponding to fourfold coordinated carbon atoms ($sp^3(C)$) are computed. The cutoff distance of 1.85 Å is used to determine the coordination number of carbon atoms. Besides, all the systems are quenched to room temperature with different quenching speeds in order to investigate the effect of quenching speeds on the structures of boron-doped ta-C. In Fig. 3(a) and (b), the symbols marked by “slow”, “standard” and “quick” show the results corresponding to quenching times from 5000 K to 3000 K in 150 fs, 100 fs and 80 fs, respectively.

As shown in Fig. 3(a), in all the three cases, the $sp^3(C)$ contents show a decrease trend as the doping content of boron increasing, which is consistent to the phenomenon of graphitization reported in the previous experimental studies [15-17]. The theoretical study by Gambirasio and Bernasconi [21] concluded that boron doping has no effect on the content of sp^3 hybridized carbon atoms. The reason why their result is inconsistent with the present one is probably that the doping content of boron in their simulations is less than 4%, and that the change of $sp^3(C)$ contents is very small within the doping content of 4% as shown in the standard case of our simulation (Fig. 3(a)).

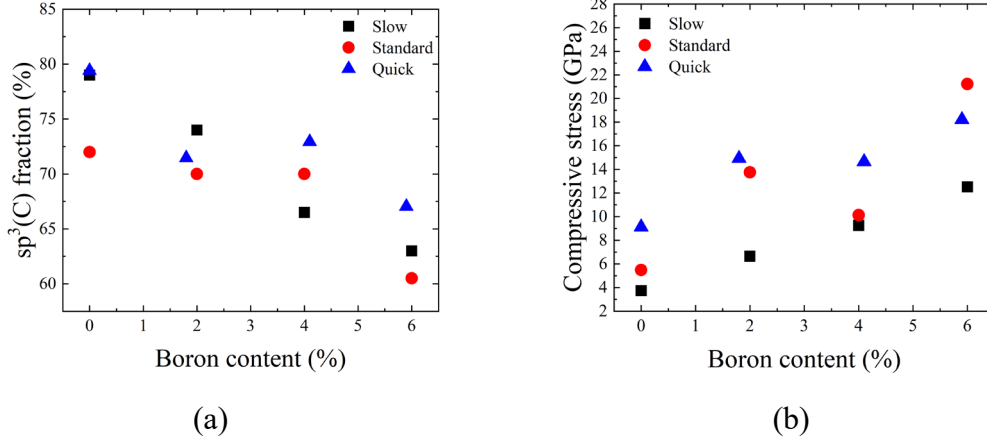


Fig. 3. Boron content dependence of (a) sp^3 content of carbon atoms and (b) compressive stress in different ta-C systems. The symbols marked as “slow”, “standard” and “quick” represent the simulation results with the time span of 150, 100 and 80 fs, respectively, for quenching from 5000 K to 3000 K.

The effects of boron doping on the internal compressive stress in ta-C are also investigated. The biaxial stress, σ , is the experimentally measured quantity, which can be calculated according to the following equations:

$$P = \frac{P_{xx} + P_{yy} + P_{zz}}{3} \quad (1)$$

$$\sigma = \frac{3}{2}P \quad (2)$$

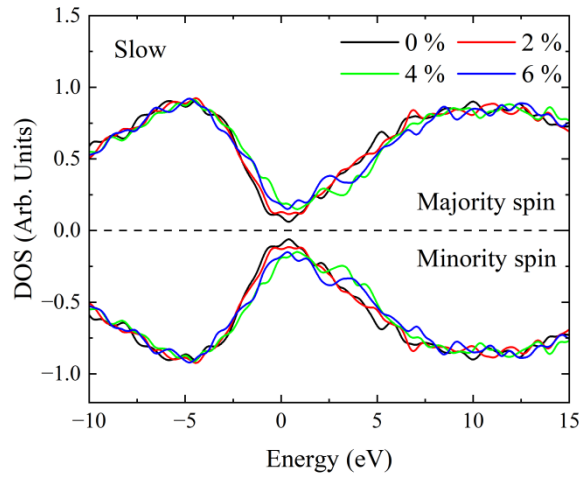
where P is hydrostatic pressure, P_{xx} , P_{yy} , P_{zz} are diagonal components of stress tensor. The biaxial stress can be calculated by multiplying a factor of 1.5 [35]. The same methods to calculate biaxial stress are also adopted in other simulations [36-38]. The changes of internal stress with the increase of boron content are shown in Fig. 3(b). Although slight oscillations are observed, the calculated internal stresses for all the three cases show the increase trends with boron content increasing. However, the previous experiments have shown that the boron doping of low content in ta-C releases internal stress [19,20]. At first glance, it seems that the results of our calculations are not in good agreement with the experimental results. This contradiction

can be solved when the approach used in our simulations is reevaluated. During each simulation, the volume of simulation box is fixed all the time. When the graphitization happens, an sp^2 site has a larger atomic volume than an sp^3 site, but the space of simulation box cannot be changed. The walls of simulation box suffer higher stresses, resulting in an increase of internal compressive stress. In other words, the increases of calculated internal stresses indicate that the graphitization is promoted by boron doping. Because the size of the box is fixed, our calculated internal stresses cannot be directly compared with actual experimental stresses. The unrealistic internal stresses calculated using fixed box also be found in previous study [39]. The more realistic calculation approach for internal stress in FPMD simulation is worth exploring in the future study. One may consider the influence of the fixed box on the other physical properties. This possibility can be ruled out. In the previous simulation study, Liu [40] relaxed the volume of box by changing its dimensions homogeneously after quenching in their first-principles calculation on amorphous carbon. The sp contents, electronic structures, and optical properties were investigated in their calculation except internal stress. They claimed that there are no obvious effects of the box size changing on the physical properties of the amorphous carbon. Based on their result, we consider that the simulation with the fixed box does not interfere with reliability regarding other physical properties.

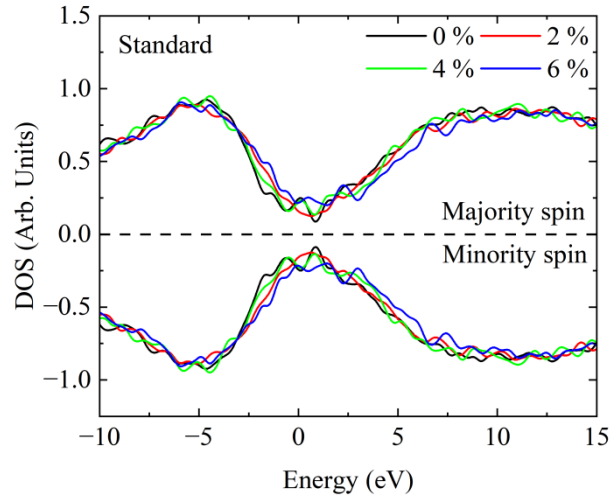
3.2 Electronic structure

Figs. 4(a), (b) and (c) show the change of the spin resolved electronic density of states (DOS) curves in the ta-C systems with the content of boron doping of 0%, 2%, 4% and 6% in slow, standard and quick cases, respectively. There are common features to be noted. Firstly, it is

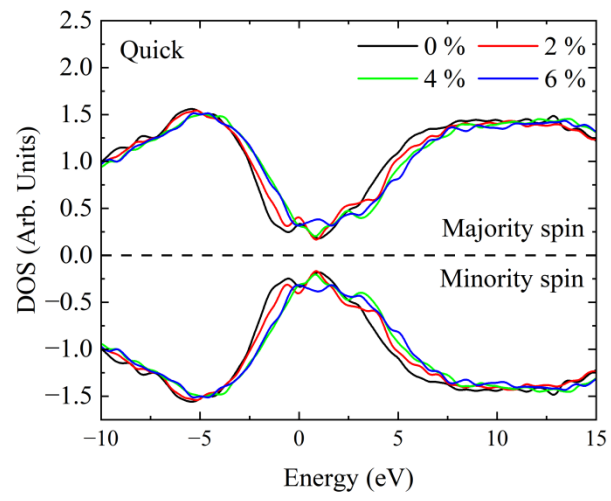
obvious to see the characteristic of amorphous structures, i.e. the electronic states consist of extended states in the bands and localized states in the middle of bands or next to band edges [41]. Secondly, the DOS curves are overall shifted to the higher energy side after boron doping, i.e. the Fermi level shifts towards the valence band. Based on the theory of semiconductor physics, the shift of the Fermi level towards the valence band indicates that boron-doped ta-C is like a p-type semiconductor. The results suggest that the existence of local states near the Fermi level have not obvious effect on the shift of the Fermi level, that is, the Fermi level pinning effect in boron-doped ta-C is relatively weak. Thirdly, an increase of intensities of the electronic states near Fermi level are found in these systems. Robertson [42] mentioned that in ta-C there exist two kinds of defects which can attribute to the states near the Fermi level. One is sp^3 dangling bonds, or isolated sp^2 sites, and another is sp^2 clusters possessing odd number of sp^2 bonded carbon atoms. Han [41] claimed that the defects consisting of isolated sp^2 atoms and odd numbered sp^2 chains will contribute to the formation of electronic states near Fermi level in the simulated ta-C structures. In our boron-doped systems, when the doped boron contents become higher, graphitization is promoted (Fig. 3(a)) and the disorder degree is enhanced in the network of sp^3 bonds. Therefore, the increase in intensities of electronic states near Fermi level is considered to be the contributions of defects due to graphitization. The shift of the Fermi level towards valence band and increase of the density of deep states in the band gap have been predicted by Kleinsorge [19] according to their experiments. Our results on the ta-C systems with the initial density of 3.0 g/cm^3 prove their claims clearly. Finally, the DOS curves corresponding to spin-up electrons and spin-down electrons are symmetric for each system, which indicate that these systems have a paramagnetic magnetism.



(a)



(b)



(c)

Fig. 4. DOS curves of simulated structures with boron concentration of 0%, 2%, 4% and 6%. (a), (b) and (c) correspond to DOS curves in slow, standard and quick cases, respectively. Two sets of DOS curves corresponding to spin-up and spin-down electrons are shown.

Projected densities of electronic states (PDOS) on C and B atoms in the ta-C system with boron content of 6% in standard case are analyzed. Fig. 5(a) and 5(b) illustrate the PDOS on C and B atoms, respectively. In both cases, the 2p states are dominant in valence bands. Because the basis set of DZVP-MOLOPT-SR-GTH includes higher angular momentum functions, d states exist in the PDOS of C or B elements. The 2p states of both C and B elements show strong intensities in the energy range from -2 to -5 eV, which indicate these two states are definitely hybridized. This phenomenon in PDOS suggests the existence of chemical bonds between C and B atoms. We also analyze PDOS with boron content of 2% and 4% in the standard case. The results are shown in Fig. S2 for boron content of 2% and in Fig. S3 for boron content of 4% in supplementary material. It is found that the intensity of PDOS curve for boron element increases with boron content increasing. However, the impact of defects is not clear and difficult to determine from these results.

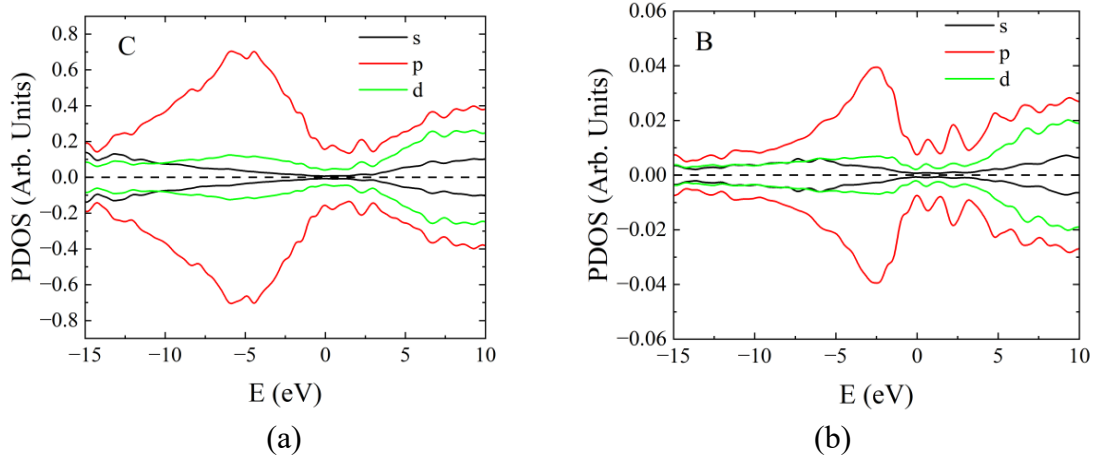


Fig. 5 Projected densities of electronic states on carbon atoms (a) and boron atoms (b) in ta-C system with boron content of 6% in standard case.

3.3 Chemical bond

The property of chemical bonds between carbon and boron atoms is further analyzed by electron density distribution. Fig. 6(a) shows the electron density distribution at iso-surface level of $0.240224 \text{ \AA}^{-3}$ in three-dimension space for the ta-C system with boron content of 6% in standard case. A special lattice plane containing three boron atoms is selected in order to analyze electron density distribution in two-dimension space (Fig. 6(b)). As seen in Fig. 6(b), there exists electron density distribution between carbon and boron atoms, indicating the formation of covalent bonds between them. Because of stronger electronegativity of carbon element, the intensities of electron density near carbon atoms are higher than that near boron atoms. The analysis for the existence of chemical bonds is consistent with the result in Fig. 4, supporting that the doped boron atoms act as a p-type acceptor in ta-C.

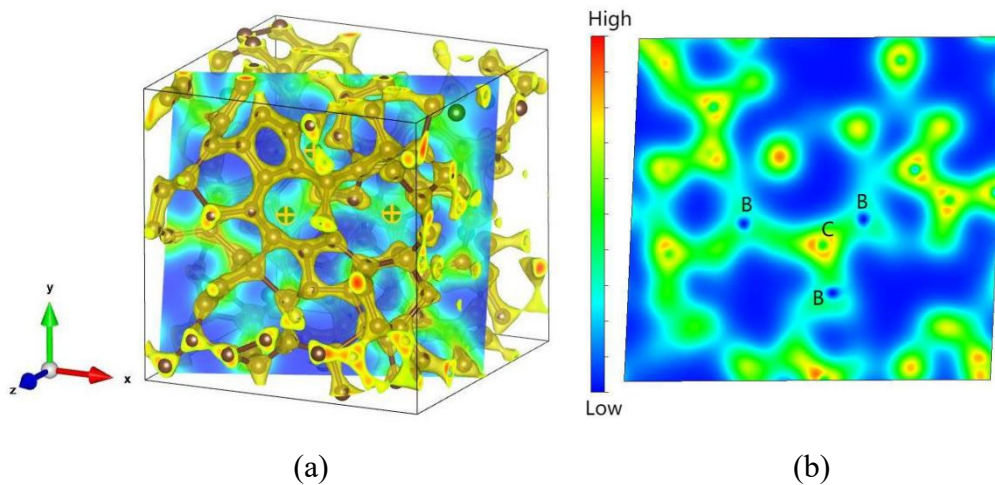


Fig. 6. Electron density distribution at iso-surface level of $0.240224 \text{ \AA}^{-3}$ in three-dimension space (a) and in two-dimension space (b) for a selected lattice plane. These figures are produced by VESTA [43].

Using FPMD simulations, the effects of boron doping on the physical properties of ta-C are presented. Our results on coordination number in ta-C are consistent with previous experimental studies. In addition, change in the electronic state with boron content varying in ta-C is, to our

best knowledge, firstly shown in our study. The shift of the Fermi level towards valence band and the formation of covalent bond between carbon and boron atoms indicate that boron-doped ta-C is like a p-type semiconductor. Due to fixed box, the calculated stress can't be compared with experimental results. Our calculation results provide useful information for determining the validity of some previous experimental results, and help deeper understand the physical properties of boron-doped ta-C. The referenced simulation methods in this study can also be used to study the effects of other dopants such as sulfur and phosphorus on ta-C and will contribute to related experimental and theoretical researches on ta-C in the future.

4. Summary and conclusion

Based on FPMD, the effects of boron doping on the physical properties of ta-C systems with an initial density of 3.0 g/cm^3 are investigated. It is found from the simulation results of bond structures and internal stress that graphitization is promoted with increase in the concentration of boron doping. Furthermore, simulation of electronic states reveals that as content of boron doping becomes larger, the Fermi level is shifted toward valence band and the intensity of electronic state near Fermi level increases. A covalent bond between carbon and boron atoms is also shown by analyzing PDOS and electron density distribution. These results indicate that boron element acts as a p-type dopant in ta-C. The present simulation results help deeply understand the physical properties of boron-doped ta-C, and also contribute to the future research in the boron-doped ta-C.

1 **Author statement**

2 Authors did not use AI and AI-assisted technologies in writing process.

3

4 **CRedit author statement**

5 **Qiang Yue:** Methodology, Investigation, Software, Data curation, Writing- Original
6 draft. **Takayoshi Yokoya:** Writing- Reviewing and Editing. **Yuji**
7 **Muraoka:** Conceptualization, Supervision, Writing- Reviewing and Editing.

8 **Declaration of interests**

9 The authors declare that they have no known competing financial interests or personal
10 relationships that could have appeared to influence the work reported in this paper.

11

12 **Acknowledgements**

13 This research was supported by JSPS KAKENHI Grant Number JP21H01624.

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