

Atomic Structure of Grain Boundaries in Diamond: A Tight-Binding Molecular Dynamics Study

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The purpose of this work is to clarify atomic and electronic structures of diamond grain boundaries and their vicinity using the tight-binding molecular dynamics (TBMD) method. As a typical coincidence grain boundary, we analyze $\Sigma=5(001)$ grain boundary, and both tilt and twist grain boundaries of $\Sigma=5(001)$ are considered. In the case of tilt grain boundary, dangling bonds disappear completely after the relaxation, while dangling bonds remain in the case of twist grain boundary. We also analyze effects of hydrogen on the structure of grain boundaries. By terminating dangling bonds with H atoms, a local transition to graphite-like structure occurs in the vicinity of $\Sigma=5(001)$ tilt grain boundary.

Key words: diamond, grain boundary, tight-binding method, molecular dynamics

1. INTRODUCTION

Diamond is one of the most attractive materials because of its transparency and high thermal conductivity. Since the CVD method became available to produce artificial diamond, applications of diamond to semiconductor devices, which can be operated at high temperature, high frequency, and high power, are studied widely. Due to further improvement of the technology, even the thickness of diamond films can be precisely adjusted.^[1] However, to apply diamond to electronic devices, we need further cost reduction by enlarging the sample size and by speeding up the processes. To achieve such a goal, one must have ability to characterize and control the structure and electronic properties of diamond interfaces. We employ the tight-binding (TB) method^{[2],[3]} to analyze atomic and electronic structure of grain boundaries in diamond.

C. H. Xu et al.^[4] has developed a TB interatomic potential for carbon in which they adopt the scaling form given by Goodwin et al.^[5] for the dependence of the hopping integrals on interatomic spacing. Their TB model is shown to have good transferability when applied to a wide variety of crystal structures: The total energy of diamond is -8.40 [eV], whereas that of graphite structure is -8.42 [eV]. These values agree very well with experimental data. We also obtain reasonable agreement with experimental values for bulk modulus and other elastic constants (C_{11} , C_{44}). Applications in molecular-dynamics studies of the liquid phase of carbon as well as the structures of small carbon clusters indicate that the potential describes carbon systems very well over a wide range of environments. Therefore, we adopt the potential model to investigate grain-boundary structure of diamond.

2. TILT GRAIN-BOUNDARY

In this section, we discuss $\Sigma=5$ tilt grain boundary of diamond. Although the $\Sigma=5(001)$ grain boundary is simple to simulate and analyze, it has a lot of defects. We first relax the grain boundary structure using TBMD method and then analyze the structure through the bond order, Mulliken charge, and density of states.

Figures 1 and 2 are the initial and relaxed stages of $\Sigma=5$ tilt grain boundary, respectively. The present model of the grain boundary can be constructed minimally with 40 atoms per unit cell. Here we use 80 atoms to analyze grain boundary of $\Sigma=5$.

Comparing Figs.1(a) and 2(a), we observe no significant displacement of atoms throughout relaxation. On the other hand, Fig. 2(b) shows large displacement of atomic layers along z direction. This is mainly due to a local reconstruction of atomic structure at the grain boundary.

In Figs. 3 and 4, we observe large fluctuations of the bond order and Mulliken charge in the vicinity of the $\Sigma=5$ tilt grain boundary. Figure 5(a) indicates that dangling-bond states exist in the initial stage. But in the relaxed stage, they disappear as shown in Fig.5(b). These observations reveal that the local reconstruction of $\Sigma=5$ tilt grain boundary, accompanying atomic-layer displacement, results in large fluctuation of electron transfer at the grain boundary.

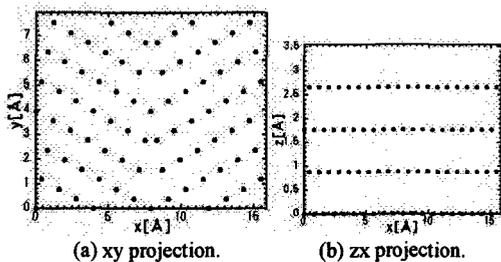


Fig. 1 Initial stage of $\Sigma=5$ tilt grain boundary.

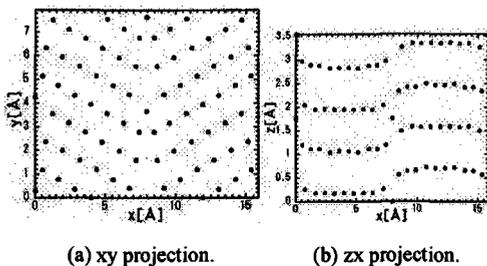


Fig. 2 Relaxed stage of $\Sigma=5$ tilt grain boundary.

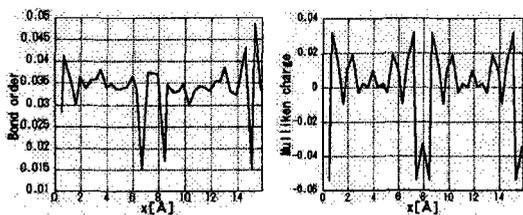


Fig. 3 Bond order(tilt). Fig. 4 Mulliken charge(tilt).

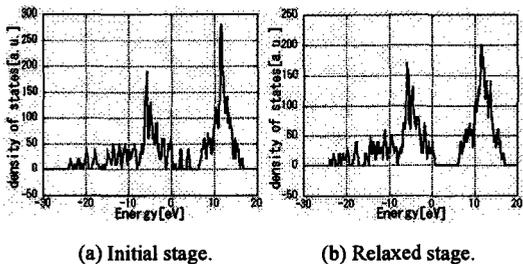


Fig. 5 Density of states(tilt).

3. TWIST GRAIN-BOUNDARY

In this section we discuss relaxation process, bond order, Mulliken charge, and density of states in the case of twist grain boundary of $\Sigma=5$. Schematic view of the system setup and atomic positions of the initial stage of $\Sigma=5$ twist boundary^[6] are shown in Fig. 6. Twist grain boundary of $\Sigma=5$ can be constructed minimally with 40 atoms per unit cell. We analyze the twist grain boundary with 160 atoms.

The initial and relaxed stages of the twist boundary are shown in Fig. 7. There are three dangling bonds in the initial stage, and these remain even after the relaxation. By effect of the relaxation, however, two or three atomic layers in the crystalline parts are largely distorted.

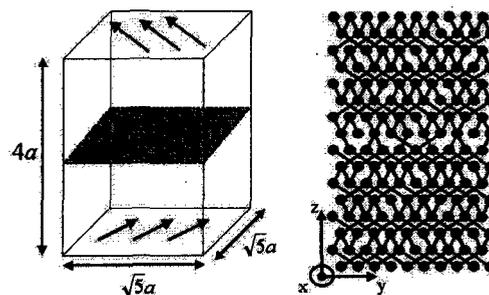


Fig. 6 Twist grain boundaries.

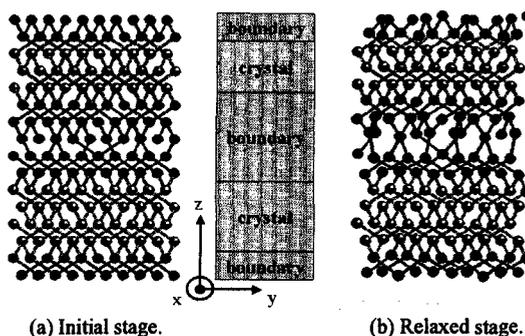


Fig. 7 Initial and relaxed stage (twist).

In Figs. 8 and 9, we see that electronic structures in crystalline parts remain rather undisturbed, in contrast to the cases of tilt grain boundary. But bond order and Mulliken charge at the grain boundary undergo large changes reflecting less adjustment of atomic layers compared to the tilt grain boundary. In Fig. 10, there are a lot of dangling-bond states in the initial stage and they remain in the relaxed stage.

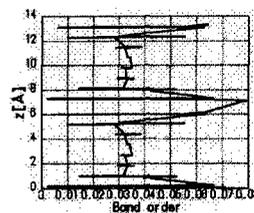


Fig. 8 Bond order(twist).

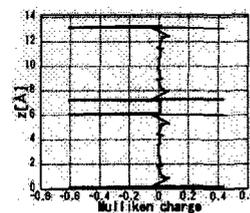


Fig. 9 Mulliken charge(twist).

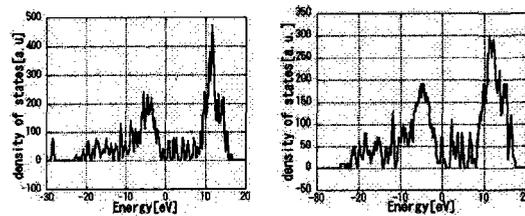


Fig. 10 Density of states (twist).

4. EFFECT OF HYDROGEN

We try to couple hydrogen with dangling bonds in the tilt grain boundary. Figure 11 shows where we terminate the dangling bond with a H atom in a grain boundary. In the initial stage of tilt grain boundary of $\Sigma=5$, where some carbon atoms have only three neighboring atoms, we place hydrogen atoms at the positions along the direction of tetrahedral structure. Bond length (0.97 Å) of this C-H pair is determined so that the potential energy has the lowest value. The system analyzed consists of 80 carbon and 8 hydrogen atoms.

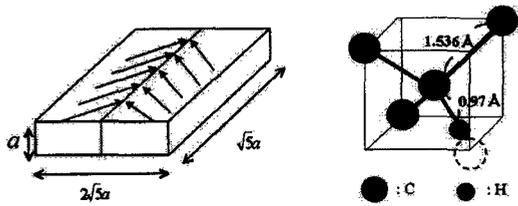
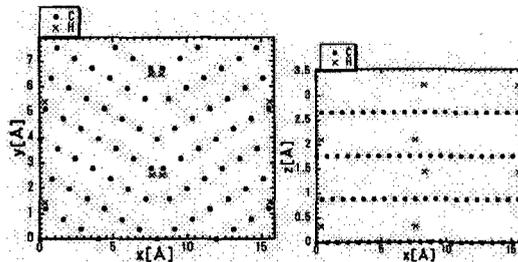
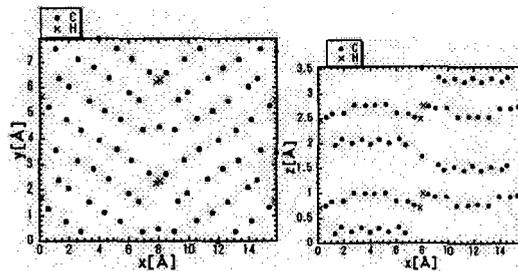


Fig.11 Model of $\Sigma=5$ tilt grain boundary (left) and relative position of H atom inserted (right).



(a) xy projection. (b) zx projection.

Fig.12 Initial stage with H atoms (cross).

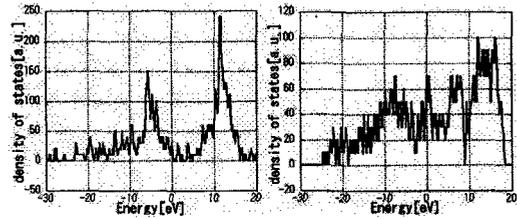


(a) xy projection. (b) zx projection.

Fig.13 Relaxed stage with H atoms (cross).

By including hydrogen, the effect of atomic-layer displacement becomes quite different from the cases without H. Interlayer distances are nonuniform in the relaxed stage, as shown in Fig.13(b).

Figure 14(a) shows that the number of dangling-bond states is decreased by including hydrogen. After the relaxation, the overall shape of the density of states is changed largely and we do not observe energy gap anymore.

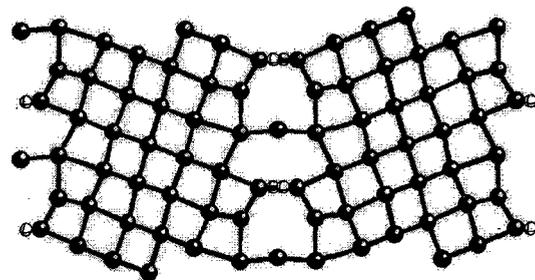


(a) Initial stage. (b) Relaxed stage.

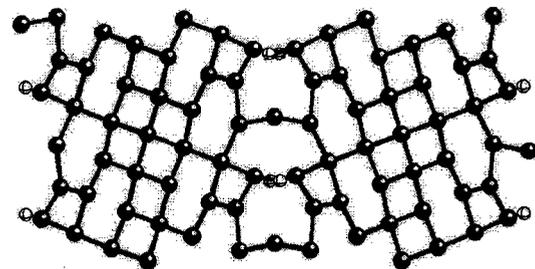
Fig.14 Density of states (with H atom).

Figures 15 and 16 show snapshots of $\Sigma=5$ grain boundary with hydrogens. The system in Fig. 15 is annealed and quenched by removing kinetic energy every 24 fs (femto second). By inserting hydrogen, diamond structure in the vicinity of grain boundary changed to graphite structure. Figure 16 shows, on the other hand, that no local transition to graphite-like structure occurs without annealing.

Table I indicates that tilt grain boundary of $\Sigma=5$ is more stable than twist grain boundary. This is the effect of large displacement of atomic layers in the case of tilt grain boundary. In the case of coupling hydrogen at the grain boundary, the energy of the relaxed stage is much lower than other cases.



(a) At 48 fs.



(b) At 97 fs.

Fig.15 The xy projection of atomic positions in relaxation process of $\Sigma=5$ tilt grain boundary with 8 hydrogen atoms (small white balls). The system is quenched by removing kinetic energy every 25 fs.

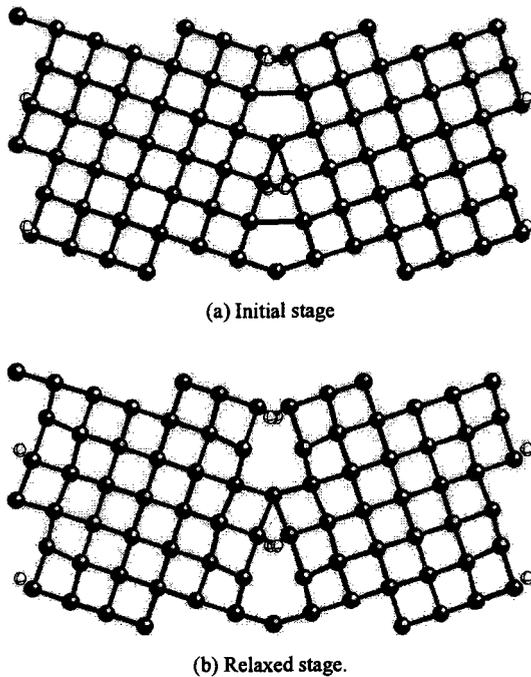


Fig.16 The xy projection of atomic positions in relaxation process of $\Sigma=5$ tilt grain boundary with 8 hydrogen atoms (small white balls). The system is relaxed by the steepest-descent method.

Table I. Comparison of energy per atom.

	Initial Stage[eV]	Relaxation Stage[eV]	Interfacial Energy* [J/m ²]
$\Sigma=5$ (tilt)	-7.69	-8.17	4.61
$\Sigma=5$ (twist)	-7.29	-7.78	9.97
$\Sigma=5 + H$ (a)	-8.08	-9.25	
$\Sigma=5 + H$ (b)	-8.08	-9.35	

*: Interfacial energy is defined here as the difference per unit area of the interface between the energy of system with grain boundary and that of perfect crystal of same size.

a: The system is relaxed by the steepest-descent method.

b: The system is annealed and quenched by removing kinetic energy every 24 fs.

5. CONCLUSION

The atomic structures of grain boundaries in diamond are analyzed using tight-binding molecular dynamics. The bond order, Mulliken charge, and density of states are calculated to characterize the electronic structures in the material. In the case of $\Sigma=5$ tilt grain boundary, dangling-bond states which exist in the initial stage almost disappear after the relaxation of the structure. Density of states of the relaxed structure is similar to bulk diamond. In the case of $\Sigma=5$ twist grain boundary, on the other hand, dangling bonds do not disappear completely. Bond order, as an index of bond strength, in $\Sigma=5$ twist grain boundary is about twice as much as that in $\Sigma=5$ tilt grain boundary. We have also analyzed $\Sigma=5$ grain boundary with hydrogen. Due to the bond

termination by hydrogen atom, the grain-boundary structure changes so drastically that structural transition takes place locally to graphite-like structure. This occurs only through dynamic relaxation and is not observed in the steepest-descent relaxation.

Further investigations are needed for systematic characterization of grain-boundary properties. To apply the present theoretical method to a variety of grain-boundary structures, more efficient algorithms^[7] need to be implemented. A parallel implementation of an order- N TBMD algorithm has already been made,^[8] and has shown to be very effective for grain-boundary analyses.

ACKNOWLEDGEMENTS

This work was supported by the Grants-in-Aid for Scientific Research (B) 11480110 and for Encouragement of Young Scientists 12750604 from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

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(Received March 8, 2002; Accepted April 30, 2002)