Role of fluctuation, disorder and catalyst in graphite-diamond transition

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Abstract

The pressure-induced structural transition from graphite to diamond is investigated by semi-empirical molecular dynamics simulation. The result shows that the graphite-diamond transition is a cooperative process with large fluctuation. We studied catalyst-aided effect by introducing a simple model into a conventional tight binding Hamiltonian of carbon bonding structure. The obtained result suggest that weak disorder in graphite not only accelerate the transition to cubic diamond but also will be an origin of high-pressure polymorph of carbon, such as hexagonal diamond.

1 Introduction

Carbon has various meta-stable polymorph, such as diamond, graphite, fullerene, or nanotube and so on. The structural transition between these polymorph structures, often induced by high pressure, has been intensively studied for years. For example, diamond is obtained from graphite by static or shock-wave compression experiments[1, 2]. The diamond obtained in such ways shows several distinct phases, such as, cubic diamond(CD) and hexagonal diamond(HD), which have different stacking and networking structures of sp3 tetrahedrons. In many cases, compressed graphite directly turns into cubic diamond with the aid of catalyst, accompanied with the change in stacking from so-called AB type into ABC one[3]. However, HD phase has also been synthesized by static compression from well-crystallized graphite[1] or shock-compression[2], in which AB stacking is kept after quenching. However, in the compression of polycrystalline graphite, no hexagonal phase is obtained[2]. It is

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also reported that the transformation to HD occurs under quasi-
hydrostatic pressure, but only CD phase is quenched[5]. Under cer-
tain conditions, ”n-diamond” phase also forms under compression
[4, 6]. There are several theoretical studies for graphite-diamond
transition from first principles. Scandolo et al. had simulated the
transformation from graphite to diamond[3]. Their simulation has
created both CD and HD structure. Tateyama et al. investigate
the activation barriers and the transition paths in the transition
to cubic or hexagonal diamond from graphite and discussed on the
origin of diamond polymorphs, which is attributed to the sliding
movement of graphite layers under compression[7]. However, from
the computational limit, the ab-initio simulations use at most tens
of atoms and they may not be sufficient for describing some as-
pect of diamond transition, since such a crystal growth process
may be subject to large scale structural fluctuation. The small size
simulation is likely to ignore that the graphite-diamond transition
shall essentially be a cooperative phenomena caused by local re-
combination of bonding structure. In addition, the realistic mech-
anism in choosing HD or CD structure under compression has not
been clarified enough by those ab-initio studies. In the present work
we adopt a tight-binding simulation using hundreds of atoms in or-
der to study possible effects in the transition, such as fluctuation,
disorder, or catalyst. At first we simulate the cooperative process
of the graphite-cubic-diamond transition. Next, the simulation for
catalyst effect in the transition to high-pressure polymorphs of di-
amond is given. There a model for catalyst-carbon combination is
included into the TB Hamiltonian for carbon bonding structure.
We propose a catalyst-aided-mechanism in the transition to carbon
polymorphs under pressure.

2 Methodology

In the simulation of pressure-induced structural transition, we adopt
a constant-pressure scheme proposed by Wentzcovitch et al.[8]. In
the evaluation of total energy and force in molecular dynamics, we
use tight binding Hamiltonian for hydro-carbon system proposed
by Winn et al.[9]. Throughout the present work, the time interval of one MD step is set to be 1fs.

In the simulation, we start with graphite structure at 0Pa. The initial stacking of graphite is set to be AB type. In case of the simulation for catalyst-aided-effect, the catalysts are randomly distributed between graphite sheets as intercalated atoms. The pressure is raised to the desired value at the rate of 1GPa/1MD steps and kept constant after that. The temperature is also kept constant. The simulation in this way does not cause any kind of abrupt change in the cell dynamics. In the constant pressure simulation[8], we set the virtual mass assigned to cell deformation heavy enough so that the inner stress shall go parallel with the increase in the external pressure.

3 Simulation of graphite-diamond transition

In this section, the result of graphite-diamond transition is shown.

In the present work, the graphite directly turns into cubic diamond at 150-200GPa and 5000-6000K. However, hexagonal phase is not obtained.

Figure 1 shows the growth of interlayer bonding between two neighboring graphite sheets. The compression process is executed at 200GPa, 6000K. The unit cell contains 12 graphite sheets with AB stacking and each graphite sheet has 40 carbon atoms. The development of interlayer bonding is estimated by the ratio defined as follows.

\[
R_{i,i+1} = \frac{2 \times (\text{Number of atoms with interlayer bonding between } i \text{ and } (i+1)-\text{th layer})}{\text{Number of atoms in a layer}}
\]

(1)

If this ratio is 0, there is no bonding structure between the corresponding two layers. On the other hand, if this ratio becomes 1, the two sheets are perfectly glued with each other by interlayer bonding.

The transition process is described as follows. When the structural fluctuation has grown enough, the diamond structure grows
very rapidly. The development of diamond structure along the c-axis is slower than that goes parallel with the original graphite plane. The domain boundaries of the diamond structure come to play a role of the mold so that they combine with nearby graphite sheet. In this way, the diamond structure will grow as a collective phenomenon. Even if the more wide graphite sheets are used in the unit cell of the MD simulation, the transition occurs similarly in the same range of the temperature and the pressure.

4 Catalyst-aided transition

In this section, the role of catalyst is investigated by the simulation including catalyst atoms, which are randomly distributed between graphite planes as intercalated atoms. In order to simulate the catalyst effect, we make use of a model, where the only s-orbital of catalyst interacts with carbon. As the tight binding parameters between carbon and catalyst, we start from those between carbon and hydrogen. We introduce a parameter λ and construct the model of catalyst-carbon coupling by multiplying λ to matrix elements and repulsion terms between hydrogen and carbon [9] in the following way.

\[ t_{sp\sigma} \Rightarrow \lambda t_{sp\sigma} \]
\[ t_{sp\pi} \Rightarrow \lambda t_{sp\pi} \]
\[ t_{ss\sigma} \Rightarrow \lambda t_{ss\sigma} \]
\[ V_{\text{rep}} \Rightarrow \lambda V_{\text{rep}} . \]

The site energy for s orbital is fixed to that of hydrogen.

The dependence of the cohesive energy and the bond length on λ in a C$_2$H$_6$ like molecule is given in figure 2.

The transition process from graphite to diamond proceeds at lower pressure and temperature with the aid of catalyst. In the present simulation, the transition temperature to diamond is 150-200GPa in the compression of genuine diamond. However, if the catalyst is induced, at most 4-6 catalyst atoms in 240 carbon atoms, and even if the catalyst-carbon coupling is not so strong (λ ≈ 0.6), the transition pressure is decreased below 100GPa. It will be attributed to the catalyst-induced buckling of the graphite basal
plane, in which $\pi$ orbitals are activated[Figure 3].

5  Formation mechanism of hexagonal diamond

A kind of stable diamond structure called as hexagonal phase is sometimes obtained by shock compression and static compression. This phase has the structural property very similar to normal cubic diamond phase. The first principle calculation shows that the cohesive energy in hexagonal phase is slightly higher than that of cubic phase[7]. In the TB model in the present work, the difference in cohesive energy between CD and HD is also very small. From the energetic viewpoint, it is also possible for hexagonal phase to be formed in the compression of graphite. However, the simulation in the former sections, generated only cubic phase. It will be attributed to the difference of the height of activation barrier[Figure 4] between the transformation paths from graphite to cubic phase and hexagonal phase, as is demonstrated by a first principles calculation [7].

According to the molecular dynamics simulation in the present work, under the presence of catalysts, the hexagonal phase is often formed, when we set certain types of initial geometry. The figure 5 shows one of the results(150GPa,6000K,$\lambda = 1.2$). The transition path to diamond phase is postulated in the following way. When cubic diamond is formed, the stacking should change from AB stacking of graphite into ABC one, as graphite sheets slide collectively. On the other hand, in hexagonal phase, the AB stacking must be kept. In the geometries under the presence of impurities, the collective slide may be disturbed and ”pinned” by the coupling between catalyst and carbon[Figure 6]. Then the short range order of hexagonal diamond is formed around the catalyst and it finally covers up whole crystal.

Figure 7 and 8 show the simulated result for a certain initial geometry with impurities. Figure 7 shows the synthesized phases after the compression as long as 2ps (2000MD steps) with various conditions for $\lambda$, and the temperature and the pressure. The simulations are started from the same initial geometry. In figure 8, in order to
investigate microscopic mechanism of the transition, the process of interlayer bonding with different conditions is shown, using plots similar to figure 1. Fig.8(a)-(c) show the formation of synthesized phases in Fig.7. The common initial configuration of impurities used in the simulation in Fig.7 and Fig.8 is given in Fig.8(d). In the simulated result, it seems that there is a certain tendency with respect to $\lambda$, temperature and pressure in the transition. In a certain range of $\lambda$ and the temperature, the transition to hexagonal phase occurs. However, if the temperature is set to be higher while $\lambda$ is fixed, the hexagonal phase tends to vanish. Instead, the transition to cubic phase occurs. When the value of $\lambda$ becomes large, the graphite turns into cubic phase, but the long range order is often damaged and large defects remain. The result of Fig.7 and Fig.8 is obtained by a set of test-run and it does not necessarily mean the phase diagram itself. However, if the different condition, such as the different initial velocity of each atom, is given, the simulation gives similar tendency when the similar initial configuration is used.

From Fig.8, the scenario of graphite-diamond transition induced by the competition of several physical conditions, i.e., temperature, pressure, presence of impurity, and so on, is described as follows.

• In the case of genuine graphite

In this case, the formation of interlayer bonding proceeds rapidly in the direction parallel with graphite plane, while it goes slowly along c-axis. In this case, the transition path to cubic phase having the lower activation barrier will be selected[Figure 4]. The simulated result shows the it costs long time before the formation of diamond structure begins. It will be interpreted to be the time lag until the compressed system will find the saddle point in the potential surface.

• Under the presence of catalyst

Since the presence of catalyst causes the combination with carbon and the buckling of graphite plane, the formation of interlayer bonding begins around impurities in earlier stage of the reaction[Figure 8(a)]. However, the catalyst is a kind of disorder and it somewhat disturbs the formation step of in-
terlayer bonding and causes the fluctuation in the cooperative transition toward cubic phase, letting down the transition speed[Figure 8(b)]. Owing to staggering in the layer-by-layer transition steps, there arises possibility of the transition to different carbon polymorph other than cubic diamond. In addition, if the sliding movement may be hindered and "pinned" by the weak coupling between catalyst and carbon, the graphite AB stacking is locally preserved, from which local core of hexagonal structure forms and finally covers the whole crystal[Figure 8(b)]. In fact, the transition to HD induced by impurities are severely dependent on randomness with respect to initial configurations of impurities and it does not always occur in the simulations like this.

- Catalyst in higher temperature

  In case of too high temperature, as the structural fluctuation of graphite sheets will exceed the catalyst-induced pinning in graphite sliding, the local core of hexagonal diamond may not be formed[Figure 8(c)]. Thus cubic diamond will form, accompanied with strain change.

- With large catalyst-carbon interaction $\lambda$

  When the $\lambda$ is set to be larger, the graphite sheets are glued firmly by impurities. Then the fluctuation in the cooperative step in the transition does not become large and the compressed graphite is rapidly stabilized into cubic phase.

  In fact, in the actual conversion process, the crystal will include various structural defects other than intercalated impurities. In the neighborhood of defects, atoms can move more freely and it will be possible for local hexagonal diamond structure to be formed out of structural fluctuation. In the simulation where the points defects are included, the short-range order similar to hexagonal phase is actually obtained.
6 Comparison to pressure-induced transition of fcc fullerene

It is demonstrated that the fullerene fcc crystal turns into transparent glassy chips of amorphous diamond phase by shock compression\cite{10}. This phase is constructed from short range order of sp$^3$ bonding and it is distinguished from normal amorphous phase of carbon. In general, amorphous carbon is interpreted to be disordered phase of graphite. By MD simulation, the pressure-induced amorphization in fullerene can also be pursued. According to the MD result, fcc fullerene collapses easily above 50GPa, 2000K and turns into amorphous phase.

Figure 9 shows the electronic structure of the finally fabricated material after the compression. These figures show the case of the following conditions, (a)65GPa,3000K,(b)125GPa,5000K, (c)125GPa,5000K with presence of 30Hydrogens. The simulation uses 240 carbon atoms , i.e., 4 C$_{60}$ molecules in a unit cell. In these figures, real and dotted lines show the total DOS and the contribution from threefold carbon, respectively. The rough feature of DOS is different to that of initial fcc fullerene\cite{11} and it is similar to that of diamond, except that gap states contributed from dangling bonds remain between valence and conduction band. If the contribution from dangling bonds between valence and conduction bands is large, the fabricated material will lose the transparent optical property and it will not be qualified to be called amorphous diamond. However, a comparison between figure 9(a) and 9(b) suggests that the contribution from dangling bonds will be reduced after the compression at sufficiently higher temperature and pressure. (In case of figure 9(a), the ratio of fourfold atom is at most 50 %. In case of figure 9(b), the ratio of fourfold atom amounts to 80 %.) The shaded zone in Fig.9(b) corresponds to the conduction-valence gap of normal diamond structure. However, gap states are still left in it. In fact, there may be other mechanism that will reduce the contribution from dangling bonds. For example, it is well-known that the presence of hydrogen atoms reduces the number of dangling bonds in case of amorphous silicon. Figure 9(c) shows the DOS under the presence of hydrogen. In this
case the ratio of fourfold carbon amounts to 60%. According to the simulations in the similar way, the number of dangling bonds decreases as the more hydrogens are doped. However, even if hydrogens are included, clear valence-conduction gap does not open because of dangling bond states. It is unlikely that a small quantity of impurities will behave as catalyst and enhance the transition to amorphous diamond, as we have seen in the previous section for the case of graphite-diamond transition. In the transition of bonding state from $sp^2$ to $sp^3$, it seems that higher pressure plays a more relevant role than the presence of hydrogen does. If the initial configuration with hydrogen, which is same as in Fig.9(c), is compressed by higher pressure (above 100GPa), the number of fourfold atom does not increase so much compared to Fig.9(a) of carbon only case.

In case of the compression of $C_{60}$, the collapsed fullerene turns into amorphous phase. Since there are number of quasi-stable configurations in amorphous phase, the transition toward diamond-like phase is very slow and the system is apt to be trapped such transient phases by quenching. As an example, figure 10 shows the two reaction path noted as (A) and (B). In both path, the pressure is increased 0Pa to 125GPa in the interval from 0.0ps to 0.5ps in the figure, and compression is executed adiabatically in the first stage. The temperature increases from initial 300K to about 2500K at the turning point of two paths. In path (A), the simulation is executed furthermore adiabatically and the temperature finally increased to 5000K. In path(B), in which the temperature is kept to 2500K, the transition to $sp^3$ bonding becomes slow due to lower temperature. Taking after different paths of(A) and (B), the system is trapped by different semi-stable configurations.

The presence of too many intermediate phase between fullerene and diamond will be a major difference to pressure-induced graphite-diamond transition. Graphite and diamond are located in very close configurations in the potential surface and there is no stable transient state in the transition path from genuine graphite to genuine diamond. Therefore graphite rapidly transforms into the cubic diamond without being trapped by any quasi-stable struc-
ture. Thus perfect diamond phase remains alone after the quenching and, in general, amorphous diamond phase will not be obtained in graphite-diamond transition. Concerning this, the role of catalyst in graphite diamond transition can also be stated in this way. The presence of impurities induces certain quasi-stable structures in the transition path from graphite. In the present simulation, such a quasi-stable structure corresponds to the local core of hexagonal diamond. Since such a quasi-stable structure staggers the transition steps from graphite, there arises possibility of transition to carbon polymorph other than cubic diamond.

7 Discussion

The present work is likely to account for some aspect of non-equilibrium process in graphite-diamond transition realized by shock compression. In shock compression, the high pressure phase, which may not have arrived equilibrium state, is quenched and frozen, since the temperature decreases very rapidly while the high pressure is still kept. In the present work, the hexagonal phase is generated as a result of non-equilibrium core formation around impurities, and such a HD phase is also stable and can be quenched. However, if the high temperature environment continues sufficiently long as is realized in the actual conversion process, and if the system will finally reach the equilibrium, the system will select cubic phase as an equilibrium phase, since cubic phase is slightly stabler than hexagonal one[7].

Several reports has demonstrated that the hexagonal diamond phase often grows in the compression of well-crystallized crystal[2, 3]. It is interpreted that the hexagonal phase is formed by the inhibited collective slide of graphite, which is caused by the difficulty of sliding movement in well-crystallized graphite[4]. However, the present work suggests that the well-crystallized property itself is not the direct origin of hexagonal phase. It would rather be attributed to weak randomness in the crystal. The presence of disorders disturbs the collective step of the transition and gives birth to the growth of the short-range order of hexagonal phase. The well-
crystallized structure of graphite helps such a short-range phase easily turn into a long-range order.

The report of the growth of hexagonal phase by static compression at low temperature\[3\] will be interpreted as the catalyst-induced ”pinning effect” to collective slide in graphite sheets. In that case, the formation of local core of hexagonal phase is not disturbed by the thermal fluctuation due to low temperature. Therefore the collective slide is inhibited and the hexagonal phase is allowed to extend. However, in the present work, the hexagonal phase does not generate in the picosecond-order simulation at low temperature. Concerning with graphite-diamond transition, Yagi et al. also reported that, when the graphite is heated by YAG laser under pressure, cubic diamond is formed instead of hexagonal phase\[12\]. This phenomena will be explained by the present simulation. Because of too high temperature, impurities does not suppress the sliding movement of graphite and the local core of hexagonal phase will not be formed.

The transition temperature and pressure in the present work are higher than those in the actual experiment of graphite-diamond transition (~20Pa, >2000K). One of the reason is as follows. The present simulation uses the perfect crystal of graphite. But the actual graphite crystal has various structural defects from which interlayer bonding will easily grow. In addition, the present simulation does not follow the shortest path from graphite to diamond. The compressed graphite drifts and fluctuates on the potential surface, and it can transform the structure only if the saddle point is find. This is different to the simulation chasing after the shortest transition path as was given in Ref.\[7\]. In the present work, large fluctuation should be grown for the compressed graphite to cross the saddle point in a finite, possibly very short, simulation time. If we use much longer simulation time, it is likely that the transition occurs in lower pressure and temperature. It may be possible that the tight-binding parameters are not accurate, since they are obtained by the fitting to graphite and diamond structure, but not fitted to the intermediate phase through transition. However, the energy difference between the intermediate phase and the cubic di-
diamond is evaluated as about 0.5-0.6 eV, which is no so different to the first principle result (∼0.4eV)[7].

An ab-initio calculation in the reference of [13] suggests that, in the compression of heavily doped GIC( LiC$_{12}$), hexagonal diamond forms in a way such that carbon cages will hold lithium in their centers. In it the c-axis of the generated hexagonal diamond is parallel to that of original GIC. The periodic distortion in graphite planes by intercalated atoms in heavily doped LiC$_{12}$ appears to be the key to diamond transition under pressure. However, such a transition path to hexagonal phase is essentially different to that suggested by the present work. In the present work, the c-axes of synthesized hexagonal diamond and those of the initial graphite are perpendicular, as are demonstrated in several experiments of hexagonal phase formation[2, 5]. In addition, the present simulation treated the case where the doping density of intercalated atom is much smaller than that of Ref.[13]. The present work suggests that randomness with respect to the initial configuration of impurities plays an essential role.

8 Summary

In the present work, we simulated diamond transformation from graphite. By compression, local core structures of diamond are formed in graphite at first. The transition proceeds collectively, accompanied with fluctuation, as the local diamond domain grows its volume by turning graphite sheets into the new boundary. In the present simulation, the genuine graphite turns only into cubic diamond, but not into hexagonal one. This will be attributed to the presence of higher activation barrier from graphite to hexagonal phase. The pressure-induced structural transition from graphite is subject to the presence of disorder, such as catalyst and possibly structural defect. We used a model which mimics the catalyst-aided diamond transformation from graphite. One of the role of the catalyst is the large reduction of transition pressure. Since the combination of carbon and catalyst causes the buckling of graphite plane where π electrons are activated, the interlayer bonding is eas-
ily formed there. At the same time, catalyst disturbs the steps of
the rapid collective transition procedure into cubic diamond. In
some cases, owing to impurities, the collective slide of graphite lay-
ers is prohibited and hexagonal diamond structure is locally formed,
from which the whole cell turns into hexagonal diamond. The sim-
ulated result suggest that ”weak disorder” will be one of the origin
of well-crystallized carbon polymorph such as hexagonal phase.

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Figure captions

- Figure 1: Interlayer bonding formation in GR-CD transition. The graphite sheets are indexed as 1, 2, .., 12 from bottom to top in the unit cell with periodic condition. The notation, for example, ”1+2”, means the interlayer bonding formation between 1st and 2nd graphite layers and so on. One graphite sheet contains 40 carbon atoms.

- Figure 2: Parameter dependence of carbon-catalyst bonding in a C₂H₆-like molecule. The bond angles are little dependent on λ.

- Figure 3: Buckling of graphite plane (gray sphere) caused by catalyst (white sphere).

- Figure 4: Activation barrier from graphite to diamond.

- Figure 5: Hexagonal diamond structure obtained by the simulation (150 GPa, 6000 K, λ = 1.2).

- Figure 6: Formation of cubic and hexagonal diamond. (a) Growth of cubic diamond. (b) Growth of hexagonal diamond.

- Figure 7: Synthesized phase after the compression with various condition, started from a certain initial geometry. (The initial geometry is given in figure 8.) The meaning of notations in the figure is as follows. GR: Graphite, CD(W): Well-crystallized cubic diamond phase, CD(D): cubic phase with large defect,
HD(W/D): Hexagonal phase, HD+CD: Coexistence of hexagonal and cubic phase. The transformed structures after MD simulations of 2ps are shown there.

- Figure 8: Formation of interlayer bonding with the presence of impurities. In each simulation, the pressure is increased from 0 to 150GPa in the first 0.15ps and kept constant after that. (a)-(c): Plot with various conditions, each of which corresponds to synthesized phases listed in figure 7. (d): Initial geometry with 6 impurities used in the simulation of figure 7 and 8. Broad lines and crosses show the relative location of 6 graphite sheets and 6 impurities in a cell. One graphite sheet includes 40 C atoms.

- Figure 9: Density of states in amorphous structures synthesized by the compression of fullerene FCC crystal. (a): DOS in the quenched structure after the compression at 3000K, 65GPa. (b): after the compression at 5500K, 125GPa. (c): after the compression at 3500K, 55GPa, with the presence of 30 hydrogen atoms among 240 carbon atoms in the unit cell. In these figures, the real and dotted lines show the total DOS and the contribution from threefold carbon, respectively.

- Figure 10: Formation of fourfold atoms in the compression of fullerene fcc cell. This figure shows the change in the ratio of fourfold carbon thorough the compression. In path (A), the simulation is executed adiabatically and the temperature increases to about 5000K. In path (B), the simulation is executes adiabatically at first, and afterwards, the temperature is kept 2500K.
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Illustration of potential surface around GR, HD, and CD

The transition path over the lower barrier is selected.

Figure 4: Activation barrier from graphite to diamond.
Figure 5: Hexagonal diamond structure obtained by the simulation (150GPa, 6000K, $\lambda = 1.2$)
Figure 6(a) Growth of cubic diamond

Graphite with AB stacking

\[ \text{Strain change} \quad \rightarrow \quad \text{Cubic diamond} \]

Figure 6(b) Growth of hexagonal diamond

Core of hexagonal phase around impurities

Figure 6: Formation of cubic and hexagonal diamond. (a) Growth of cubic diamond (b) Growth of hexagonal diamond.
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DOS (states/eV/C atom) vs $E_F$

(c) 3500K, 55GPa, 30H/240C

ENERGY (eV)

0 5 10 15 20
Formation of fourfold carbon

Figure 10: Formation of fourfold atoms in the compression of fullerene fcc cell. This figure shows the change in the ratio of fourfold carbon thorough the compression. In path (A), the simulation is executed adiabatically and the temperature increases to about 5000K. In path (B), the simulation is executes adiabatically at first, and afterwards, the temperature is kept 2500K.