

Large scale simulation of quantum-mechanical molecular dynamics for nano-polycrystalline diamond

Takeo Hoshi^{1,2,3}, Toshiaki Iitaka³ and Maria Fyta⁴

(1) Department of Applied Mathematics and Physics, Tottori University, 4-101 Koyama-Minami, Tottori 680-8552, Japan

(2) Core Research for Evolutional Science and Technology, Japan Science and Technology Agency (CREST-JST), Japan

(3) RIKEN (The Institute of Physical and Chemical Research), 2-1, Hirosawa, Wako, Saitama 351-0198, Japan.

(4) Physics Department, Technical University of Munich, James Franck Strasse, 85748 Garching, Germany.

E-mail: hoshi@damp.tottori-u.ac.jp

Abstract. Quantum-mechanical molecular-dynamics simulations are carried out to explore possible precursor states of nano-polycrystalline diamond, a novel ultra-hard material produced directly from graphite. Large-scale simulation with 10^5 atoms is realized by using the ‘order- N ’ simulation code ‘ELSESES’ (<http://www.elses.jp>). The simulation starts with a diamond structure that contains initial structural defects and results in a mixture of graphite(sp^2)-like and diamond(sp^3)-like regions as nano-meter-scale domains. We speculate that the domains are metastable and are possible candidates of the precursor structures.

1. Introduction

Nano-polycrystalline diamond, a novel ultra-hard material, is produced directly from graphite at high temperature and high pressure and is of great interest both for fundamental science and industrial applications. [1, 2] Nano-polycrystalline diamond consists of fine diamond crystals of 10-30 nm in size and has a characteristic lamellar structure in the 10 nm scale. Its precursor structure is crucial for the controllability of the growth process and the functions of nano-polycrystalline diamond and was investigated, for example, in a recent experiment. [3]

In the present paper, nano-polycrystalline diamond is explored by large-scale simulations based on quantum mechanical molecular dynamics [4, 5, 6, 7, 8], with up to 10^5 atoms. The aim is to find candidates of intrinsic precursor structures of nano-polycrystalline diamond, which cannot be achieved in smaller scale simulations. The present work is the first stage for simulating a controllable growth process, since a simulation of growth process requires proper initial structures and intrinsic precursors will give such initial structures.

2. Method

The large-scale simulations were realized by an ‘order- N ’ electronic structure calculation based on Krylov subspace theory, in which the computational time scales linearly with the system size. [5, 6, 7] In the Krylov subspace theory, the Green’s function is calculated, instead of eigenstates.

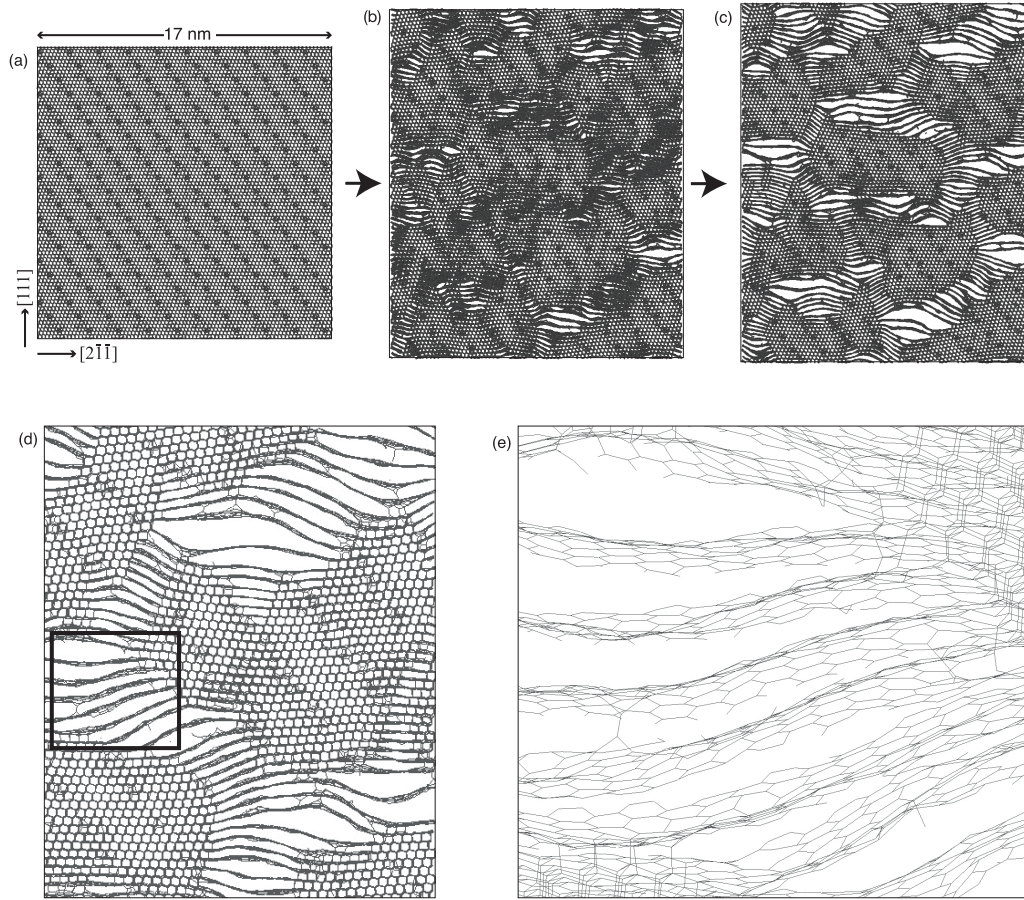


Figure 1. (a)-(c): Successive snapshots of a simulation with 107,520 atoms under the [111] tension, at time steps 0, 720 and 820. (d): Close up of the upper right region of (c). (e): Close up of a graphite-like region shown by the rectangular box in (d). A diamond-like region appears in the upper right area. The view point in (e) is slightly tilted from the one in (a)-(c).

The methodology has a rigorous mathematical foundation as iterative linear-algebraic algorithms and is applicable to both insulators and metals.

In general, an ‘order- N ’ calculation is represented in real-space. The one-body density matrix is defined as

$$\rho(\vec{r}, \vec{r}') \equiv \sum_i f_i \phi_i^*(\vec{r}) \phi_i(\vec{r}'), \quad (1)$$

with eigenstates $\{\phi_i\}$ and occupation numbers f_i , where \vec{r}, \vec{r}' are the positions. Then the expectation value of a physical quantity $\langle X \rangle$ is calculated by

$$\langle X \rangle = \text{Tr}[\rho X] = \int \int \rho(\vec{r}', \vec{r})^* X(\vec{r}, \vec{r}') d\vec{r} d\vec{r}'. \quad (2)$$

In the Krylov subspace theory, the Green’s function $G = G(\vec{r}, \vec{r}'; \varepsilon)$ is calculated by an iterative algorithm and the density matrix is given by

$$\rho(\vec{r}, \vec{r}') = -\frac{1}{\pi} \int f(\varepsilon) \text{Im} [G(\vec{r}, \vec{r}'; \varepsilon + i0)] d\varepsilon \quad (3)$$

where ε is the energy and $f(\varepsilon)$ is the occupation number given by the Fermi-Dirac function. Now the simulation code is being reorganized as a package with the name ‘ELSESES’ (=Extra-Large-Scale Electronic Structure calculations). [4] The complete reference list of ELSESES for its methodology and application is found in a recent paper. [8] In this paper, a tight-binding form Hamiltonian for carbon [9] is used. The methodological details of the Krylov subspace theory in the present simulation are the same as those for liquid carbon. [7]

In the first stage of our research, the simulations were carried out by expanding a diamond structure with initial structural defects, a small fraction of threefold-coordinated atoms and deformed fourfold-coordinated atoms, not more than 10 %. In this way, we aim to obtain the intrinsic metastable structures of nano domains within the limit of the computational time scales. Three-dimensional periodic simulation cells are used for the samples. The samples were prepared as super cells of smaller samples with initially structural defects. [10] The procedure of generating the initial structure is given in a paper [11] The computational time with 107,520 atoms is typically 20-23 minutes per molecular-dynamics step on a standard workstation that has two quad-core Intel Xeon^(TM) processors (E5345, 2.33GHz).

3. Results and discussion

Figure 1 shows a simulation result with 107,520 atoms under the [111] tension. The snapshots of Fig. 1[(a),(b),(c)] correspond to the initial, 720-th and 820-th steps, respectively. The time interval per molecular-dynamics step is $\Delta t = 3$ fs and the last step corresponds to the elapse time of approximately 2.5 ps. An orthorhombic cell is used as the periodic simulation cell and the initial cell lengths are 17.4, 17.6 and 2.0 nm along the [111], $[2\bar{1}\bar{1}]$ and $[01\bar{1}]$ directions, respectively. Fig. 1 depicts the atoms in the simulation cell with a viewpoint along the $[01\bar{1}]$ direction. The [111] tension is realized by expanding the cell size only for the [111] direction. The cell length is expanded by $0.03L_0$ every 100 steps, where $L_0 = 17.4$ nm is the initial length. The structure relaxation for given cell lengths was carried out under thermal fluctuations, introduced by a Nosé thermostat [12]. The temperature of the thermostat is set to be $T = 600$ K.

The simulation resulted in a mixture of graphite-like regions in the sp^2 state and diamond-like regions in the sp^3 state, as in Fig. 1(c). Several initial defects introduce graphite-like regions, since defective regions are relatively unstable and easier to be transformed into other stable or metastable forms. The graphite-like sheets are perpendicular to the [111] direction and are "wavy" and the diamond-like domains have several characteristic domain shapes. Similar domain shapes are formed in simulations with smaller numbers of atoms ($10^3 - 10^4$ atoms) and a longer time scale (10^1 ps). We speculate that these domain structures are metastable and are candidates of possible nano-polycrystalline domains or their precursor structures.

Simulations were carried out also under the [001] tension to confirm that graphite-like regions appear not only under the [111] tension. Figure 2 shows a simulation with 4,608 atoms under the [001] tension. An orthorhombic cell is used as the periodic simulation cell and the initial cell lengths are 4.3, 4.3 and 1.4 nm along the [100], [010] and [001] directions, respectively. The time interval per molecular-dynamics step is $\Delta t = 3$ fs. The [001] tension is realized by expanding the cell size only along the [001] direction. The cell length is expanded by $0.01L_0$ every 100 steps, where $L_0 = 4.3$ nm is the initial length. Fig. 2 [(a),(b),(c)] correspond to the 2500-th, 2,900-th and 3,500-th steps, respectively. In the last snapshot, Fig. 2(c), several graphite-like six-member rings appear at the right lower region.

In summary, we have shown that the order- N electronic structure theory realizes large-scale calculations with 10^5 atoms on a standard workstation and can play a crucial role in the investigation of nano-polycrystalline diamond. In the future, a more systematic investigation, with quantitative analysis of atomic and electronic structures, will be carried out to serve as a direct comparison with experiments.

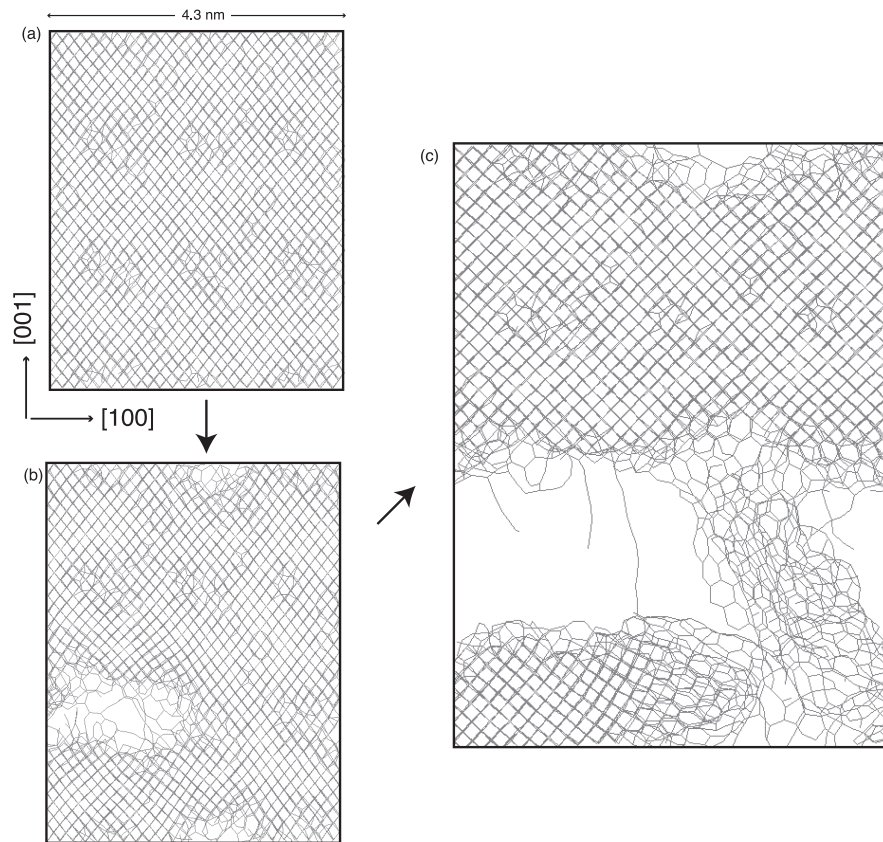


Figure 2. (a)-(c): Successive snapshots of a simulation with 4,608 atoms under the [001] tension, at time steps 2,500, 2,900 and 3,500. The last snapshot (c) is magnified by 50 % in its size to clarify the structure.

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