Large Scale Simulations for Carbon Nanotubes

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Nano carbon materials as nanotubes (CNTs) and fullerenes in nanotechnology have a lot of potential for industrial applications. On the efforts of developing applications, it has been recognized that computational simulations are powerful and efficient tools to find and create new materials from nano scale.

Aiming at realistic simulations for nonmaterial, we have developed a large-scale computation technique utilizing tight-binding molecular dynamic method, *ab initio* density functional theory (DFT), and time-dependent DFT method.

We have studies various physical properties of nano-carbon and applications e.g., (1) Ultra-fast carrier dynamics in carbon nanotubeshot carrier dynamics, (2) High-energy and Highly charged ion-collision to graphite and subsequent structural change, (3) Atomic and Electronic Structures of CNT-Metal Contacts, (4) Generation of new atomic structure using GSW rearrangement, (5) Superconducting transition temperatures of hole-doped diamonds. In addition to nano carbon as nanotube, diamond and graphite of traditional carbon material came into limelight.

Along these works, we have realized that the Earth Simulator is a very powerful tool for large-scale material simulations.

Keywords: Large scale simulation, TB theory, *ab initio* theory, DFT, Carbon Nanotube, Fullerenes

1. INTRODUCTION

Carbon materials have been expected to make a breakthrough in material science and nanotechnology. A lot of potential applications of nanotubes and fullerenes e.g., electronic field emitter and electronic devices have attracted scientific community. In the investigation and utilizing their material properties, numerical simulation using supercomputer has turned to be a very efficient tool. A recent development in nanotechnology has required a more efficient supercomputing capable of a large-scale simulation of up to 10^4 atoms.

Aiming large-scale simulations utilizing Earth Simulator, we have developed computational package based on *ab initio* DFT theory and parameterized tight-binding (TB) method. The TB code we have developed is shown to be suitable for the very large systems even though the lack of symmetrical arrangement. We have carried out some subjects in this work, which are described in the next section. There are three primary objectives with this work: (1) design of innovative nonmaterial with certain desired properties; (2) obtaining fundamental properties in nano-scale matter, and (3) nano-applications. Our purpose is to give the clear explanation of properties and phenomena of nano-scale events and deduce guiding principle to design new materials for applications from nanostructures using super-computers.

2. PHYSICAL STUDIES ON NANOMATERIALS

2.1 Ultra-fast carrier dynamics in carbon nanotubes

Last year, we demonstrated rapid reduction of electron-hole energy gap in the (3, 3) nanotube and the temperature dependence of carrier decay, which manifested an existence of electron-electron and electron-phonon time domains in the (3, 3) nanotube. These findings give important knowledge on application to high-speed optical and electronic devices. The computational method is a combination of the time-depend-

ent density functional theory (TDDFT) being coupled with the molecular dynamics (MD), which enables us to simultaneously treat electron-dynamics and ion dynamics.

This year, we have found that the decay dynamics depends on nanotube chi rarity. The figure 1 shows time-evolution of electron and hole energy levels for (3, 3) nanotube (left) and the (7, 0) nanotube (right). One can clearly notice significant reduction of the electron-hole energy gap in the (3, 0) nanotube while such reduction is not the case in the (7, 0) nanotube. This fact suggests an efficient light radiation only from semiconducting nanotubes. Although the excited electron-hole pair is stable in the (7, 0) nanotube, we expect that presence of defect or impurity may cause rapid reduction of the energy gap because of induction of defect- or impurity-induced energy levels near the Fermi level. This is our near-future plan of investigation.

2.2 High-energy and Highly charged ion-collision to graphite and subsequent structural change

We explore the possibility of changing the structure of conventional graphite by smashing highly-charged ions. Possibility of graphite-diamond conversion by irradiating Ar^{+8} ions was reported by Meguro et al. [See, Appl. Phys. Lett. 79. 3866 (2001).] Motivated by this experiment, we investigated the high-energy Ar^{+8} ion collision on the surface of graphite. Our computational model consists of four-layer graphite sheets in the AB stacking. We smashed a center of a C-C- bond on the first layer by an Ar^{+8} ion with kinetic energy of 400 eV.

Figure 2 shows the snapshots of atomic geometry and charge density upon collision of an Ar^{+8} ion. Two major events are rapid charge transfer from graphite to the ion before collision and formation of sp^3-like bond formation later the collision. These two events were monitored by the TDDFT-MD simulation. Surprisingly, the incident Ar^{+8}, which was almost neutralized after the collision, were stopped in between the first and second layer despite its heavy mass (more than twice of that of C atom) and high kinetic energy. The structural change is expected to be sensitive to the incident energy which is now under investigation.

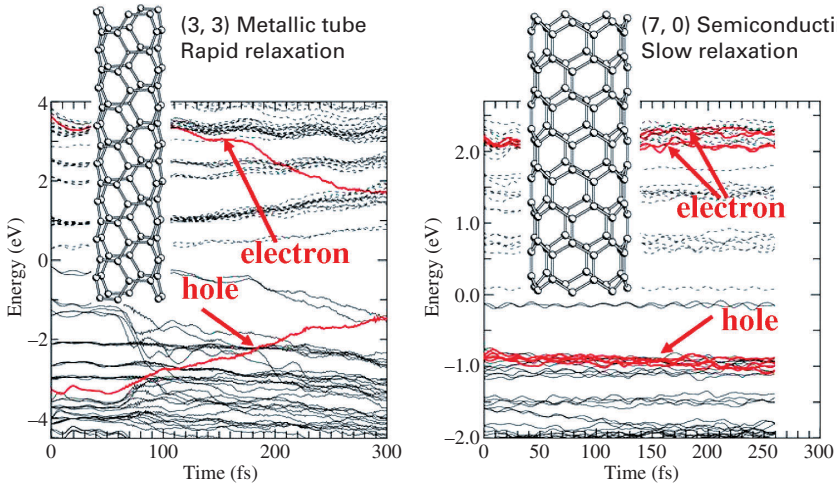

Fig. 1 Time-evolution of excited electron-hole pairs in (left) (3, 3) nanotube and (right) (7, 0) nanotubes. The insets are atomic geometries of the nanotubes.

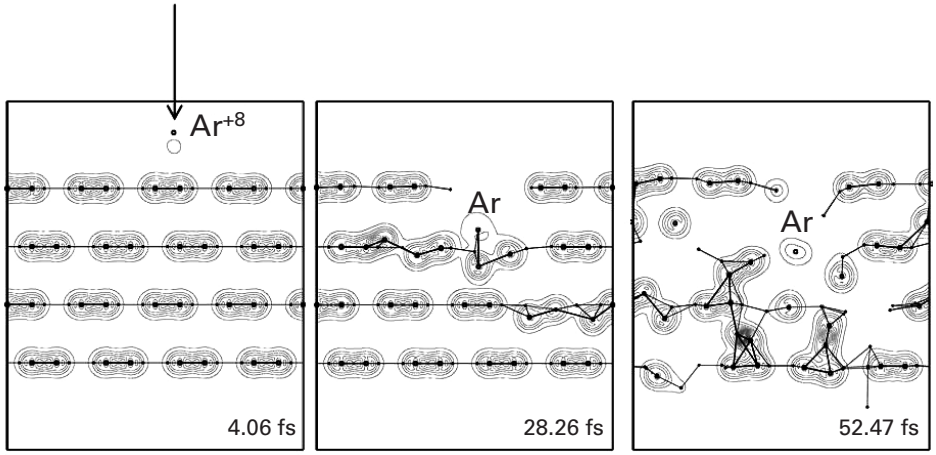

Fig. 2 Snapshots of collision of an Ar^{+8} ion on graphene layers. The contour lines are valence charge density showing rapid charge transfer from graphene sheet to the Ar ion prior to the collision. The right-most column shows appearance of sp^3-like bonds, which may indicate formation of nano-diamond.

2.3 Atomic and Electronic Structures of CNT-Metal Contacts

Carbon nanotubes (CNTs) have shown potential properties for electronic devices. The contacts with the metal, however, have not been understood enough. The atomic and electronic structures of CNT-metal contacts have been studied by using ab-initio molecular dynamics. We have examined titanium (Ti) and molybdenum (Mo) as possible contact materials. When the unit length of the model is 2 nm (90 carbon atoms and 96 metal atoms in a unit cell), the optimization is unable to keep the interface for both of the metals. The contacts show the clear difference between the metals by enlarging the model to 4 nm (170 carbon atoms and 216 metal atoms in a unit cell). For CNT-Ti, only metal atoms in the outermost layer move by optimization from the initial simple contact. For CNT-Mo, all metal atoms show remarkable change in their positions. We can obtain the local densities of states near the Fermi level accounting for electric conductance. This suggests that Ti is better as a contact material and that we need larger-scale calculations than the forecast to discuss the properties of nano-contact structures.

2.4 Generation of new atomic structure using GSW rearrangement

The purpose of this research is to find out more energetically stable and useful structure from a certain given initial state (including fullerene, CNT and nano particle) by using only Generalized Stone-Wales (GSW) rearrangement. In the simulation, the initial structure generates a huge number of topologically different or new ones by means of GSW rearrangement until the generation should be stored in a database. Searching for all the paths, with the help of capability the large-scale parallel computer, is executed along master/slave type parallel program in which a processor operates as master and the other processors as slave. The slave calculates the energy of new structure generated by GSW rearrangement and the master gathers all of data calculated by slaves and classifies them. In accordance with gathering data, next GSW rearrangement's structures being calculated is send to slaves. We achieved the high performance computing through the processors of 512 nodes.

Figure 4 illustrates snapshots of isomerization from (8, 1) CNT to (5, 4) CNT and (10, 3) CNT, and Figure 5 shows the corresponding energy of each step. It is confirmed that the (8, 1) CNT can isomerize to two types of CNT with a different chirality and radius. We guess that the intermediate structure (for example, B and D in Fig. 4) change to CNTs (for example, C and F in Fig. 4) by self-organization because the energy of intermediate structure is higher than one of CNTs.

One-dimensional problem such as CNT has been dealt with in the simulation. As a next target, we are challenging to three-dimensional problem in Fig. 6. It is a simulation whether the path from the structure connected by C60 to three-dimensional Mackay structure exists or not. In this simulation the objective nano particle is assumed to be consists of hexagon and heptagon. Figure 6 exhibits snapshots of the intermediate generation process. The future work will analyze the process to generate Mackay structure that has been predicted to be stable but not been produced yet.

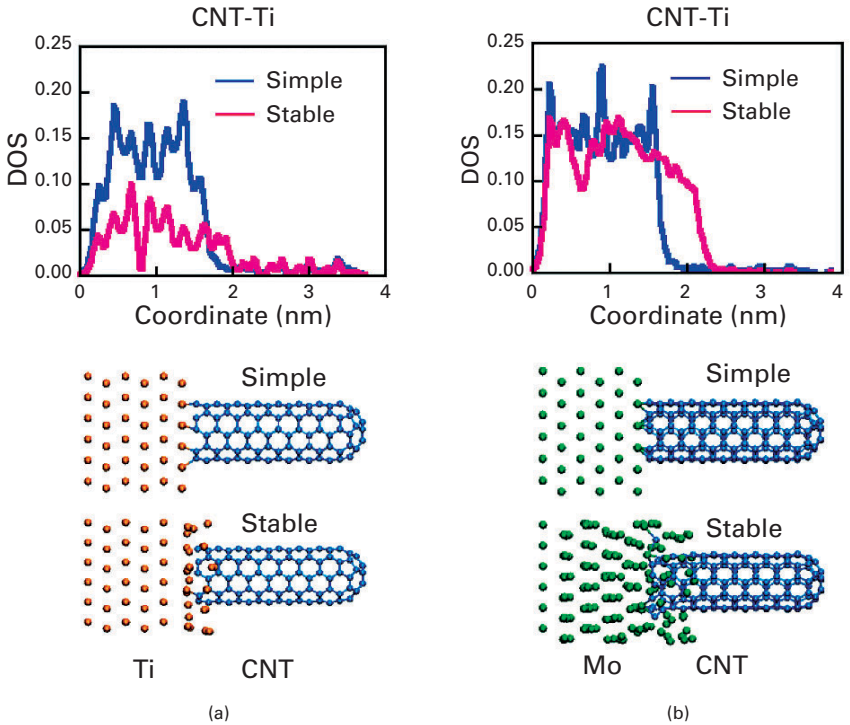

Fig. 3 Simple and stable structures of CNT-Ti (a) and CNT-Mo (b) contact and local density of states accounting for electric conductance.

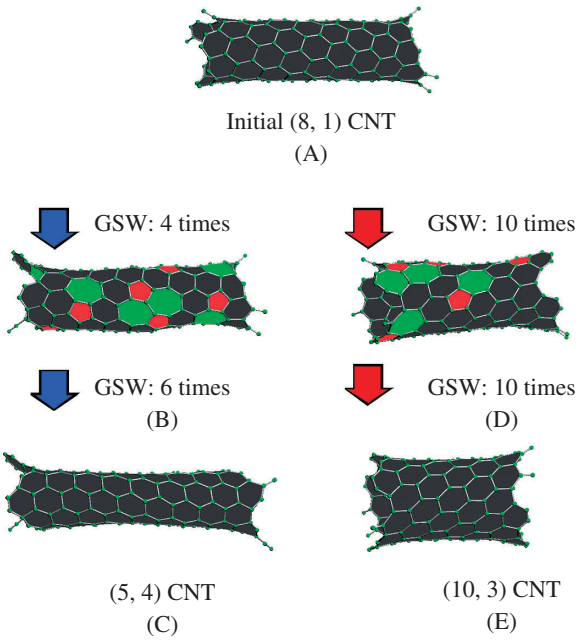

Fig. 4 Snapshots of isomerization from (8, 1) CNT to (5, 4) CNT and (10, 3) CNT.

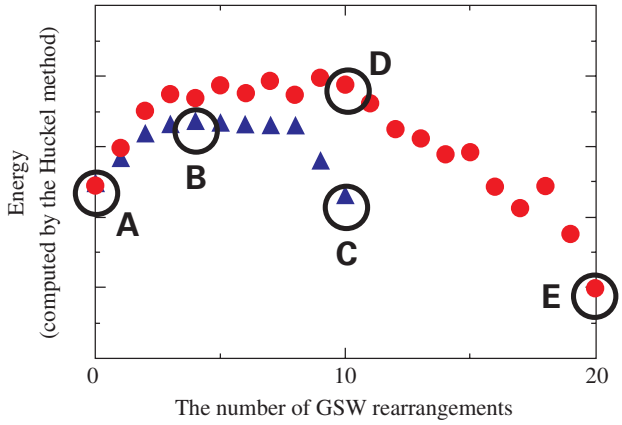

Fig. 5 Energy of each step.

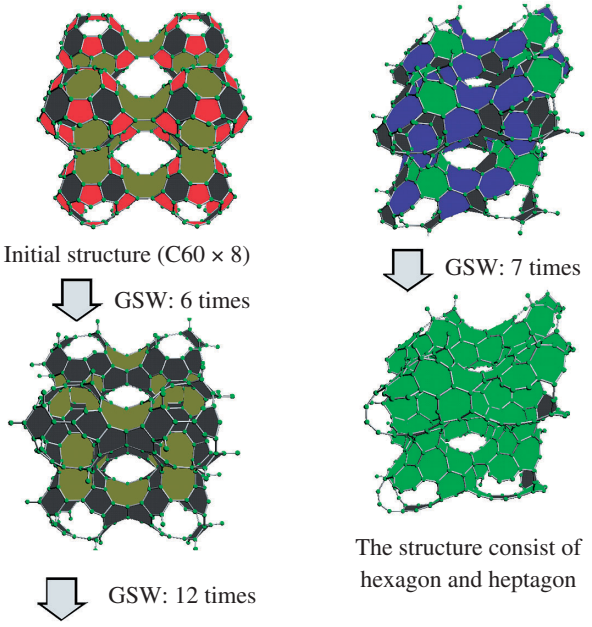

Fig. 6 Snapshot of the generation process.

2.5 Superconducting transition temperatures of hole-doped diamonds

The development of the room temperature superconductor would be a key for human to solve human race's energy problems. The conventional superconductivity can be understood by the electron-phonon pairing mechanism. Recently the spin fluctuation mechanism for the superconductivity has attracted attention as a promising mechanism for the high temperature superconductivity of cuprates. However, the recent experimental results indicate that the charge fluctuation is surprisingly large and may be possibly responsible for the pairing mechanism. From the point, Tachiki *et.al*. have proposed a new mechanism of superconductivity due to charge fluctuation. The central concept of their theory is that electron-electron interaction via strong charge fluctuation mediated by phonon can result in attractive force between electrons. We propose here that the charge fluctuation mechanism is applicable to hole-doped diamond superconductor which is currently attracting considerable attention. Hole-doped diamond has the strong electron-phonon interaction and is considered to be highly correlated electron system as expected from the insulation of pure diamond. Therefore, according to the charge fluctuation mechanism, hole-doped diamond is a strong candidate for a high temperature superconductor.

Diamond, when it is heavily doped with boron, becomes superconducting with reports as high as 12 K. However, impurities such as boron are known to suppress *T*c due to Abrikosov-Gor'kov pair breaking. Our aim is to study by simulation experiment that at what temperature hole-doped diamond becomes superconducting if holes are doped into diamond without using impurities.

To this end, we have simulated the time evolution of displacement $\delta\boldsymbol{u}(t)$ of the C atoms relative to the equilibrium position by using tight-binding molecular dynamics code for large scale simulation. In the present simulation, the number of C atoms in the diamond is 512 and the simulation of $\delta\boldsymbol{u}(t)$ is performed up to 4ps with 8,000 time steps. Using the time-series date of $\delta\boldsymbol{u}(t)$, we can obtain the dielectric function through the linear-response theory. Figure 1 shows an example of the frequency dependence of the dielectric function for $\boldsymbol{q} = (0.25, 0, 0)\pi/a$, a being the lattice constant. One can note that the dielectric function becomes negative in the wide range around $\omega = 0$. The longitudinal optical phonon changes the transfer integrals for electrons, since the phonon amplitude in diamond is very large, and also holes weaken the bond strength between carbons. Especially, when $(\boldsymbol{q}, \omega)$ component of the dielectric function is near the longitudinal phonon dispersion curve, the electron-motion is resonantly modified and the dielectric function becomes negative due to the overscreening effect.

The Fourier component of the effective interaction $V_{\text{eff}}(\boldsymbol{q}, \omega)$ is written as $4\pi e^2/[q^2\varepsilon(\boldsymbol{q}, \omega)]$., where $\varepsilon(\boldsymbol{q}, \omega)$ is the dielectric

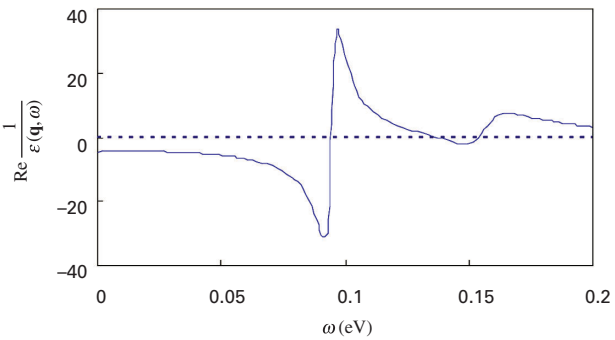

Fig. 7 Real part of dielectric function versus ω for q = (0.25, 0, 0) π/a.

function. From the above result $V_{eff}(\boldsymbol{q}, \omega)$ becomes negative and the strong attractive force appears between electrons. *T*c is determined as the temperature below which the linearized gap equation for the anormalous Green's function has a nontrivial solution. By solving the linearized gap equation with $V_{eff}(\boldsymbol{q}, \omega)$ numerically, we obtained that *T*c is about 260 *K* for diamond with 0.2 holes per carbon atom. While in our calculation the Brillouin zone is divided into 4 × 4 × 2 equal cubes and the number of samplings of data is 4, they are not large enough to get statistically meaningful ensemble average for temperature. However, our result suggests that hole-doping to pure diamonds makes them high temperature superconductors. Henceforth, in addition to improving the precision of our numerical computation, we will incorporate the effect of self-energy for the single-particle Green's function.

3. SUMMARY

The large-scale simulations on nonmaterial have been carried out by *ab initio* density functional method and the parameterized tight-binding calculations. The optimized codes showed that the computation on the Earth Simulator could give an exceptional performance and enables us more chance for large-scale and realistic simulations. Our large scale simulations can provide the nanotechnology industries valuable information on novel nano material properties and on nano electrical designs for application.

References

[1] Y. Miyamoto, Simulation of excited state dynamics in nanotubes with use of the Earth Simulator, Computational Challenges and Tools for Nanotubes, 26 JUN 2005, Chalmers University of Technology, Göteborg, Sweden.

[2] S. Tejima, Large-scale simulations for nanocarbons, Computational Challenges and Tools for Nanotubes, 26 JUN 2005, Chalmers University of Technology, Göteborg, Sweden.

[3] Y. Miyamoto, Ultra-fast Dynamics in Carbon Nanotubes Explored by the Earth Simulator, The 3rd Nano-Simulation Technology Workshop, Nov 24 2005, Mita, Tokyo, Japan.

[4] S. Tejima, Large-Scale Nano Carbon Simulation, The 3rd Nano-Simulation Technology Workshop, Nov 24 2005, Mita, Tokyo, Japan.

[5] S. Tejima, K. Minami, M. Iizuka and H. Nakamura, Large-scale simulation on Carbon Nanotubes, The Japan Society of Applied Physics, Vol.74, No.8, p.1045–1051 (2005).

[6] M. Tachiki and S. Nakamura, International Workshop on Superconductivity in Diamond and Related Materials, 08 DEC 2005, NIMS, Tsukuba, Japan.

カーボンナノチューブの特性に関する大規模シミュレーション

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概要

1. 研究目的

優れた物性と予想されナノテクの基本材とされるカーボンナノチューブ(CNT)類の電子・機械特性を従来不可能だった大規模シミュレーションにより推定し、科学技術及び産業界に提供すると共に、応用として特性の優れた新構造を発見し、基本材の拡充に寄与する目的で実施された。

2. 成果

H14年度、地球シミュレータを利用した大規模シミュレーションの有効性を世界に先駆けて実証した。またH15・H16年度は、我が国のナノチューブ研究で当面する課題解決に向けた応用シミュレーションを実施した。本年度さらに、応用シミュレーションを推進し得られた成果を以下に示す。(1)次世代回路応用特性把握の面において昨年度は、高速デバイス応用に重要な知見を与える、(3, 3)ナノチューブのキャリアーの緩和過程での電子-電子相互作用と電子-格子相互作用による2つの時定数の存在を示した。本年度は、その緩和過程がナノチューブのカイラリティと励起のエネルギーに依存することを見出した。またナノチューブ・金属結合の電子特性シミュレーションを実施し、解析規模が結果に与える影響を調べ大規模解析の必要性を明らかにした。さらに必要性が判明した規模で大規模シミュレーションを実施し、金属種の違いによる電子伝導性の違いが明らかにされた。(2)新物質創製のためのナノ構造加工特性把握の面から、GSW理論(一般ストーン・ウェルズ理論)による炭素原子の結合変換過程シミュレーション法を高速化し地球シミュレータ上で512ノードが使用可能となった。この高速版GSWコードを使用し、初期CNTから径や螺旋度の異なるCNTへの変換の可能性をシミュレーションし、(8, 1)CNTから(5, 4)CNTや(10, 3)CNTへ変化するパスが存在する事が分かった。さらにC60を組み合わせてマッカイ構造を創成するパスを発見するシミュレーションを実施中である。またナノ構造加工の面について、グラファイト多層膜に、Arイオン照射を行いダイヤモンド構造を見出したという実験(理研)についてシミュレーション追試を行った。グラファイトの予想外の頑丈さと、sp3構造に類似した結合の存在を明らかにしたが、ダイアモンド変態を結論付けるまでには達していない。(4)基本特性の面からは、ダイヤモンド薄膜などのナノ炭素構造に超伝導性の可能性が予想されるため、新しい高温超伝導メカニズムを提案し、理論シミュレーションを実施した。

キーワード：大規模シミュレーション，タイトバインディング理論，アビニシオ理論，密度汎関数法，カーボンナノチューブ，
ナノダイヤモンド