# Large Scale Simulations for Carbon Nanotubes

Project Representative
Kazuo Minami Research Organization for Information Science & Technology

Authors
Syogo Tejima *1, Kazuo Minami *1, Satoshi Nakamura *1, Kohji Makino *1,
Yoshiyuki Miyamoto *2, Mari Ohfuti *3, Mamoru Sakaue *3,
Yoshikazu Fujisawa *4 and Hisashi Nakamura *1

*1 Research Organization for Information Science &Technology (RIST)
*2 Fundamental and Environmental Research Laboratories, NEC Corporation
*3 Nanotechnology Research Center, Fujitsu Laboratories Ltd.
*4 Honda R&D Co., Ltd.

CARBON NANOTUBE RESARCH GROUPE
Morinobu Endo, Eiji Osawa, Atushi Oshiyama, Yasumasa Kanada, Susumu Saito,
Riichiro Saito, Hisanori Shinohara, David Tomanek, Tsuneo Hirano, Shigeo Maruyama,
Kazuyuki Watanabe, Takahisa Ohno, Yoshiyuki Miyamoto, Hisashi Nakamura

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), GSW rearrangement and time-dependent DFT method. We have studies various physical properties of nano-carbon and applications e.g., (1) Nano-structural deformation by ion irradiation, (2) Atomic and Electronic Structures of Contact between Carbon Nanotube and Titanium, (3) Generation of new atomic structure using GSW rearrangement, (4) Composite material formed from twisted CNTs, (5) Hole-doped diamond superconductor. 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, GSW, Hole-doped Diamond superconductor

## 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. The Eliashberg equation linearized with respect to the anomalous Green's function applied to the prediction of high Tc superconductivity for a hole-doped diamond. The Generalized Stone-Wales (GSW) rearrangement is used to find new novel nano carbon structures. 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 Nano-structural deformation by ion irradiation

Ion beam irradiation is one of important technology for nano-scale fabrication. The structural deformation from graphite to nano-diamond upon irradiation of $Ar^{8+}$ ion (high-charged ion) was suggested by the RIKEN group [1]. Motivated by this report, the mechanisms of the structural change are studied by means of electron-ion dynamics. Experimentalists of RIKEN thought that the high charge of Ar is essential to determine the structure, and thus they expected that the resulting structure appearing on the graphite surface was independent on the $Ar^{8+}$ incident energy. From theoretical point of view, speed of electron flow from graphite and Ar ion should be a key factor during the collision, thus electron dynamics in addition to MD should play very important roles.

Last year, we investigated the structural deformation by first-principles electron-ion dynamics simulation based on the time-dependent density functional theory (TDDFT) coupled with Ehrenfest approximation for classical MD. We set the incident energy of $Ar^{8+}$ ion as 400 eV, the same value as that in experiment, and found significant destruction of graphitic structure causing transient formation of local $sp^3$ configuration.

This year, we examined the dependence of the structural deformation on the incident energy by testing several values as 40 eV, 125 eV and 225 eV. In sharp contrast to experimentalists' expectation, the resulting geometry is highly dependent on the incident energy of $Ar^{8+}$[3].

Figure 1 shows how resulting geometries differ. In case of $Ar^{8+}$ irradiation with incident energy of 40 eV, the Ar ion is simply reflected dressing electron cloud and graphite retains its honeycomb network. When incident energy is increased as 125 eV, single vacancies are formed not only on the graphene surface layer but also on the third layer below the surface. The most interesting structural change is seen when the incident energy is 225 eV. The simulation shows roll-up structure of graphene sheet obtained by connecting the third and fourth layers.

Figure 2 (a) shows more detailed viewgraph of the final geometry in Fig. 1 obtained with incident energy of 225 eV.

One can be interested in how this rolled geometry sustains until the system is cooled down. Figure 2 (b) shows how kinetic energies of C atoms are distributed after the collision of $Ar^{8+}$ ion on the graphene layers. Surprisingly, even in short time constant as 0.1 ps (100fs), the kinetic energy distribution on each carbon layers seems to be equal suggesting semi-equilibrium condition. The estimated temperature for

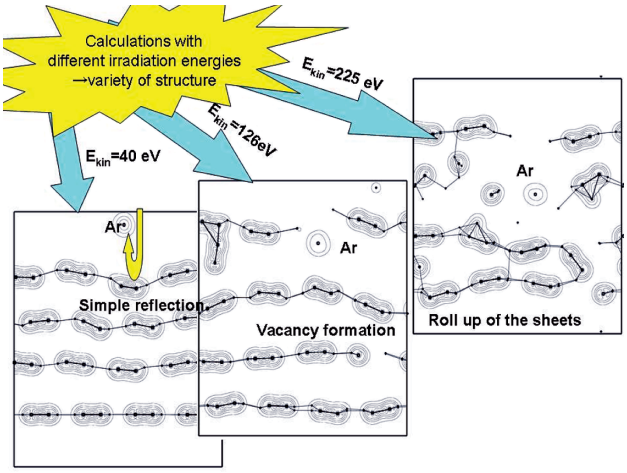


Fig. 1 Varieties of structures obtained upon $Ar^{8+}$ irradiation with several incident energies denoted in each panel. The charge contour maps are also shown indicating semi-neutralization of $Ar^{8+}$ ion in each case.

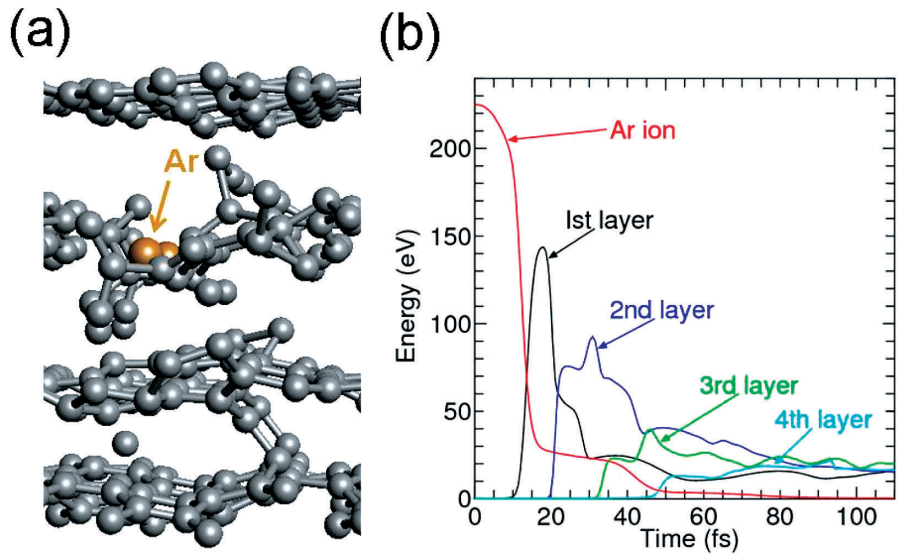


Fig. 2 (a) The modified structure of graphene sheets irradiated by an $Ar^{+8}$ ion with incident energy of 225 eV. (b) The corresponding distribution of kinetic energies of Ar ions, of C atoms in the 1st, 2nd, 3rd, and 4th layers, as a function of time.

each layer is around 3100 K but should be lower when thicker model are available to test. We thus expect formation of rolled structure is very likely.

In next year, we will examine effect of the charge on Ar ions by comparing current results with the cases of neutral Ar irradiation.

### 2.2 Atomic and Electronic Structures of Contact between Carbon Nanotube and Titanium

For electronics applications of carbon nanotubes (CNTs) the contact with metal is important. We have studied the atomic and electronic structures of the contact between metallic nanotube and titanium (Ti) as a possible contact material by using ab-initio molecular dynamics (Fig. 3). The atomic structure was stabilized from the simple contact by the Ti atoms sticking out around the CNT. The Ti and C atoms have been found to form the structure like a TiC nanoparticle. The electronic structure has also changed especially near the Fermi level, where the more charge is distribute to the contact layers and the CNT than the simple contact. This suggests that Ti plays the role as a contact material.

### 2.3 Generation of new atomic structure using GSW rearrangement

The purpose of the research is to search for the possibility of the creation of new novel nano carbon structures by using only Generalized Stone-Wales (GSW) rearrangement. We have explored the procedure of sequential GSW rearrangement (it is named to "path".) from initial structure to objective structure. The various kinds of paths were found out. For example, one was the path from 2 connected C60 to short CNT, another was the path from a certain CNT to other CNT that has different chirality, and so on.

In this report, the objective structure is periodic carbon structure with hexagon and octagon rings of carbon, known as P-surface of Schwarzites. The structure is very interesting for many researchers, and is analyzed the characteristics in the simulations, because it has negative curves and high symmetry. However, the procedures of the generation have not been clarified yet. Two types of the P surface have been known. One is called as P688, the other is P8BAL. The number of atoms per primitive cell of P688 is 48. The cell of P8BAL consists of 192 atoms. Furthermore, we discover the

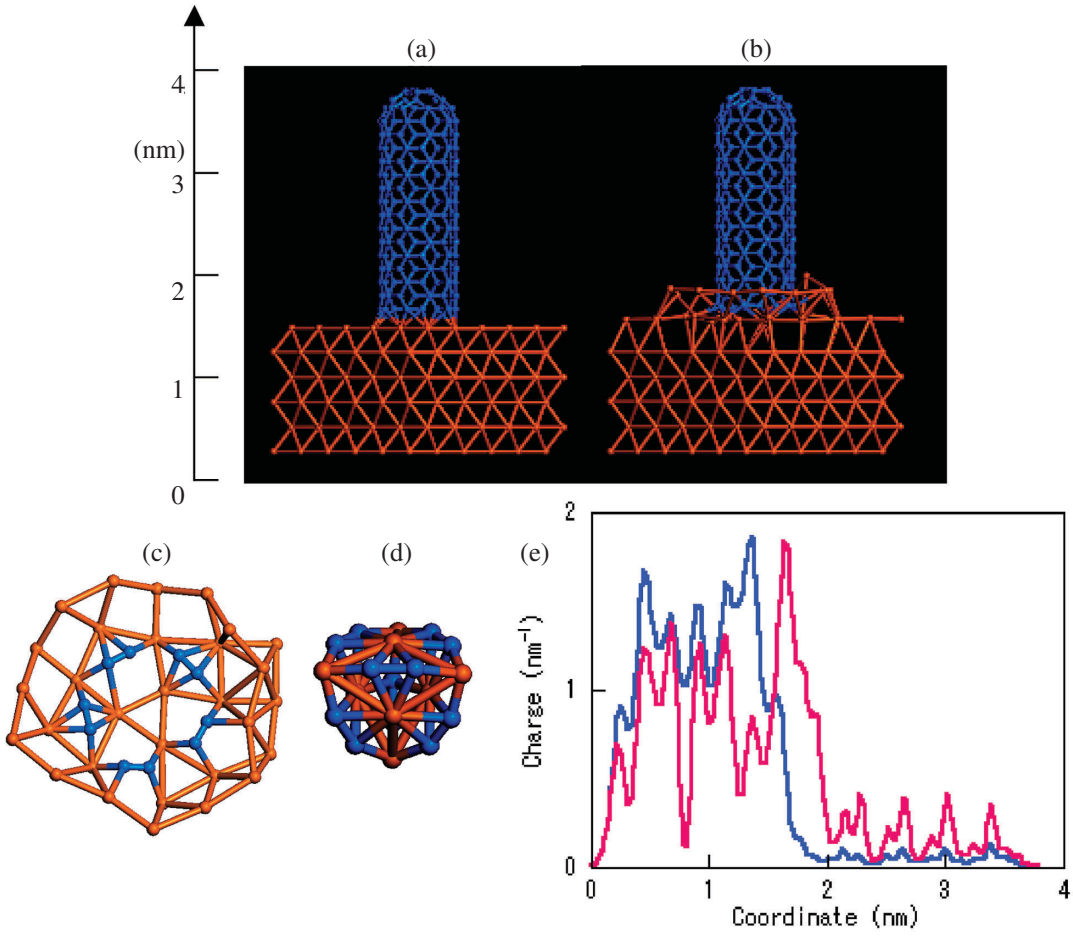


Fig. 3 (a) Simple and (b) stabilized atomic structures of the contact between carbon nanotube (CNT) and titanium (Ti). The blue and orange spheres represent C and Ti atoms, respectively. (c) Nanoparticle-like structure at the root of the CNT and (d) the $Ti_8C_{12}$ nanoparticle. (e) Initial (blue) and stabilized (red) charge distributions near the Fermi level along the tube direction.

structure that consists of 144 atoms per cell. This report deals with two types (P688 and the new structure with 144 atoms) of three, because P8BAL is too large to be explored all the paths by this program. It is assumed that initial structure is (8, 8) CNTs that are connected with 4 CNTs. The difference of them is a distance of the connecting position. First, in the case of P688, snapshot are shown in Fig. 4. 16 GSW steps are necessary for isomerization. Secondly, Fig. 5 illustrates snapshot of isomerization of another objective structure. The isomerization is realized by 164 GSW steps. Though this report deals with only P-surface, there are G and D surfaces and they have interesting characteristics as well as P-surface. In the next step of the research, the paths to these surfaces will be found out.

2.4 Composite material formed from twisted CNTs

The aim in this section is to present a design for strong and functional composite materials formed from CNT. We have been investigating mechanical properties of nano carbon structure from basic structures as a single CNT and multi-CNT to complex structures as a composite CNT. The characteristic structure and properties of single and multi CNTs play an important role in synthesizing more complex composite materials. Therefore, stage by stage, we launched our simulations.

Two years ago, we presented a the technique to create CNTs in the bundles using van-del walls attractive interaction. But the interaction is too week to remain CNT bundle under even low temperatures.

In expectation of creating atomic bonding between CNTs to keep bundle, we tried to twist the CNTs presented in Fig. 6.

Because of the torque caused by twisted CNTs, CNTs in the bundles at the initial state changed to come loose under the free edgy. So as to hold CNTs twisted under the free edgy condition, we have to induce atomic bonding between CNTs. From the results of any trial simulations, we found the suitable condition of applied temperature and a rate of twist per length to generate atomic bonding between CNTs.

The $sp^3$ hybridization bonding appears on the surface of CNTs. Three orbitals contribute to intra atomic bonding and

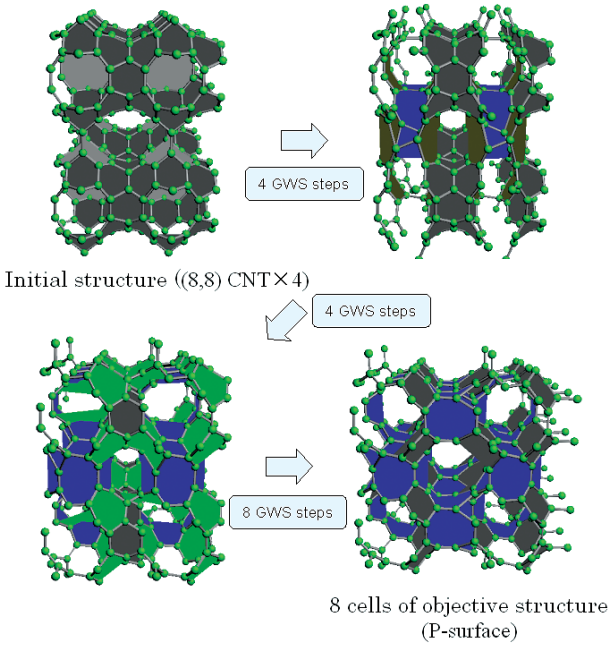


Fig. 4 Snapshot of isomerization (P688).

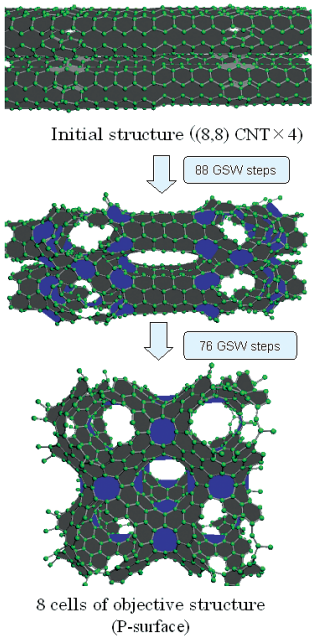


Fig. 5 Snapshot of isomerization
(Structure consisting of 144 atoms per cell).

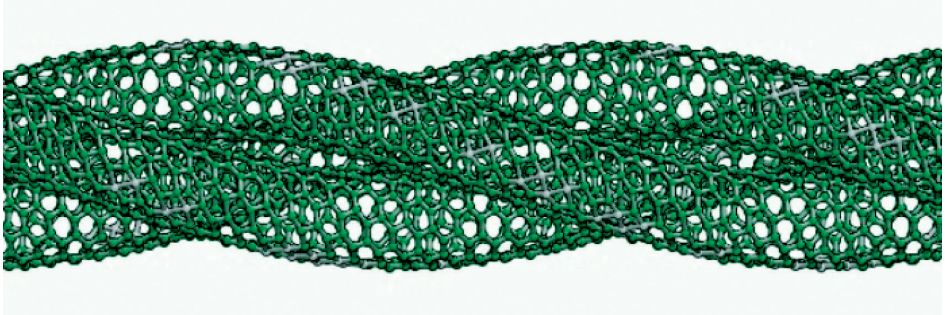

Fig. 6 Rope of nanotube.

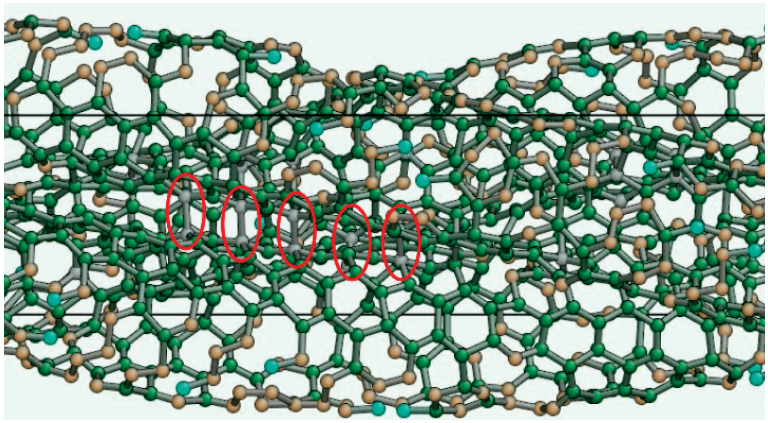

Fig. 7 The sp3 hybridization between CNTs.

one orbital to inter atomic bonding presented in Fig. 7. As a result, $sp^3$ hybridization might prevent CNTs in the bundles from coming loose. But for a long time simulation the site of atomic bonding rearrange on the surface. The most important thing in this simulation is that there is no impurity with the exception of Carbon in the structure. So we think the structure expressed here is one of the stronger structures among the composite material formed from pure CNTs.

2.5 hole-doped diamond superconductor

Recently, hole-doped diamonds have attracted considerable attention. Our aim is to investigate by simulation experiment that at what temperature hole-doped diamond becomes superconducting if holes are ideally doped into pure diamond without using impurities. To this end, we have formulated from microscopic point of view a general non-perturbation scheme of the calculation of dielectric response functions. Specifically, we simulated the time evolution of charge density r(t) of the carbon atoms using PVCRTMD (Parallel Vector Carbon Recursion Technique Molecular Dynamics) code for order-N tight-Binding molecular dynamics simulation. In the present simulation, the number of carbon atoms in the diamond was 4096 and the simulation of the charge density. $\rho$(t) was performed up to 8.2 ps with 0.5 fs time step. The sustained performance of 4.82 Tflops was achieved by utilizing 130 nodes (1040 PEs) of the Earth Simulator.

From the simulated charge density $\rho$(t), the dielectric response function is given by adopting the linear-response theory. And also the effective interaction between electrons is defined as a bare Coulomb interaction divided by response function. Thus, solving the Eliashberg equation with the effective interaction, we can obtaine the relation between the hole concentration and $T_c$.

Since we is concerned with $T_c$ , the Eliashberg equation is linearized with respect to the anomalous Green's function. Then, the Eliashberg equation reduces to a eigenvalue problem: MX=$\lambda$X, where M is a function of the single Green's

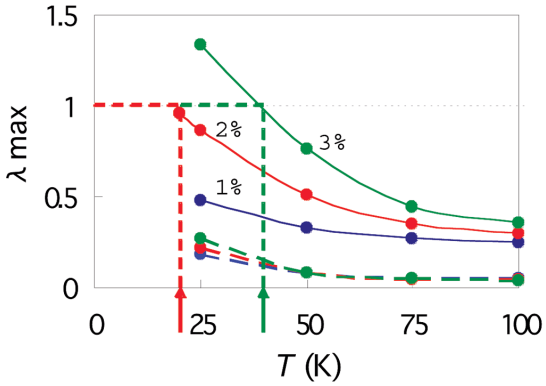


Fig. 8 Eigenvalues for the linearized Eliashberg equation are plotted as functions of temperature.

function and effective interaction, and X corresponds to gap function. $T_c$ is determined as the temperature at which the largest eigenvalue $\lambda_{max}$ of the kernel M crosses 1. From Fig. 8 we see that the attractive interaction between electrons occurs due to strong interplay between electrons and lattice vibration. We also see that $T_c$ suddenly increases with hole concentration.

The results of our simulation show that hole-doped diamond within a rigid-band approach is promising superconductor. We hope that the results presented here could stimulate further experimental work on the synthesis and characterization of diamond into which holes are ideally injected with no impurity.

## 3. SUMMARY

The large-scale simulations on nonmaterial have been carriedout by *ab initio* density functional method and the parameterizedtight-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.

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# 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

プロジェクト責任者
南　　一生　　財団法人　高度情報科学技術研究機構

著者
手島　正吾*1，南　　一生*1，中村　　賢*1，牧野　浩二*1，宮本　良之*2，大淵　真理*3，坂上　　護*3，
藤澤　義和*4，中村　　壽*1

*1　財団法人　高度情報科学技術研究機構
*2　NECラボラトリーズ　基礎研究所CNT応用研究センター
*3　株式会社　富士通研究所
*4　株式会社　本田技術研究所

## 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・H17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、カーボンナノチューブを極細配線材とする場合、ナノチューブと金属の界面では原子が混ざり合い電子伝導に影響することを明らかにした。また金属の種類によっても性質が異なること、さらに最適金属候補を選択しCNTと金属界面について構造を初めて安定化し、そのときの電子状態から金属電極の有効性とその機構に対する知見を得た。(2)新物質創製のためのナノ構造加工特性把握の面から昨年度は、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ノードを使用可能とした。本年度は、世界中で生成過程を開発できていない高強度、磁性体のマッカイ構造について、従来推測されていた規則配列したC60からの生成過程では難しく、むしろ重合したナノチューブからC144のマッカイ構造を合成できる形成経路がある事を明らかにした。またナノ構造加工の面について、昨年度に引き続き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。本年度は、実験家達の間で重要視されていなかったイオンの入射エネルギーも、イオン照射後引き続いて起こる、グラファイト表面下に起こす、構造変化を決定付ける重要なファクターであることを明らかにした(入射エネルギーが400eVではダイアモンド様な$sp^3$結合、225 eVでは、グラファイト層を丸めたような構造が発現)。ナノダイアモンドから、フラーレン・ナノチューブの初期構造まで多様なナノ炭素構造を成長させるきっかけとなる構造を作れることがわかってきた。さらに新奇機能物質の面から、ダイヤモンド構造を拘束機能としたナノチューブバンドル構造の可能性を大規模シミュレーションから発見し、長尺ナノチューブ複合機能構造の可能性を提示した。(4)基本特性の面から昨年度は、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。本年度は、そのシミュレーションを進め現実的なホール濃度での超伝導転移温度を推定した。

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