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, Yoshikazu Fujisawa*3 and Hisashi Nakamura*1

*1 Research Organization for Information Science &Technology (RIST)

*2 Fundamental and Environmental Research Laboratories, NEC Corporation

*3 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, Yoshikazu Fujisawa, 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), Generalized Stone-Wales (GSW) rearrangement and time-dependent DFT method. We have studied various physical properties of nano-carbon and applications e.g., (1) Electron-ion dynamics under time-varying external field, (2) Generation of Mackay structure by using GSW rearrangements, (3) Hydrogen adsorption to Transition-metal -decorated CNT, (4) Growth Mechanism of CNT, (5) Hole-doped diamond superconductor.

In addition to nano carbon as nanotube, diamond and graphite of traditional carbon material were also highlighted. 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, CNT growth, Hydrogen storage, 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 being 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 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 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 Electron-ion dynamics under time-varying external field

By means of the TDDFT, we have developed a computer code for electron-ion dynamics (electron dynamics coupled with molecular dynamics) in materials *under time-varying external electric field*. The code originates from currently used TDDFT code, which was used for exploring excited state dynamics in carbon nanotube with use of the Earth Simulator. The new code can include time-varying external field beyond perturbation theory which can be applied for a situation of irradiation with strong and short pulse of laser beam.

Although there already been couples of trials simulating electron-ion dynamics under time-varying external field, the numerical accuracy in simulation has not been checked clearly. In this work, we have found criteria which can guarantee numerical accuracy and stability throughout the simulation by the energy conservation rule. In the molecular dynamics (MD) simulation, the summation of potential and kinetic energies of all ions (called as U later) must be conserved. This is also the case in electron-ion dynamics. When a time-varying external field is applied to the system, the quantity U should increase due to the work done by the external field. The amount of the increase must be dependent on the time-dependence and the strength of the external field as well as intrinsic energy spectrum of the material.

We have found that the amount of increase U can simply be expressed by following equation within a framework of TDDFT, where the external field is expressed by the Hartree potential generated by fictitiously introduced charge density $\rho_{ext}(\vec{r})$ mimicking the external field.

$$\frac{dU}{dt} = \iint \frac{d\rho_{ext}(\vec{r'},t)}{dt} \cdot \frac{\rho_{ext}(\vec{r},t) + \rho(\vec{r},t)}{|\vec{r'} - \vec{r}|} d\vec{r} d\vec{r'} + \sum_I \int \frac{d\rho_{ext}(\vec{r},t)}{dt} \cdot \frac{Z_I}{|\vec{r} - \vec{R}_I(t)|} d\vec{r}$$

Here, $\rho(\vec{r})$ means electron charge and Z_I means charge of ion I, while $\vec{r}$ and $\vec{R}_I(t)$ mean coordinates of electrons and ions, respectively. By integrating the above equation with respect to time-axis, the work given by external field is computed and the subtraction of the work from U must be constant.

Next, we demonstrate the numerical stability of our computer code by simulating energy accumulation in graphite layers by pulse laser. Here the maximum strength of the electric field is hundred times bigger than typical values of the scanning microscope spectroscopy such as 10 eV/Å. Figure 1(a) shows contour lines of external potential varying along with a direction normal to the graphite layers. Figure 1(b) shows time-dependence of the external-field shown in Fig. 1(a), which is a combination of Gaussian and sin curves. With this applied external field, the energy increase of graphite is observed up to the simulation time of 6 fs. The computed size contains 80 carbon atoms with the slab geometry including vacuum region of 10 Å. Figure 2 shows that the energy conservation rule still works even with this unusually strong external field showing robustness of the numerical accuracy in our computer code. With use of currently developed code, we will investigate response of nanocarbons against irradiation with the Femtosecond laser

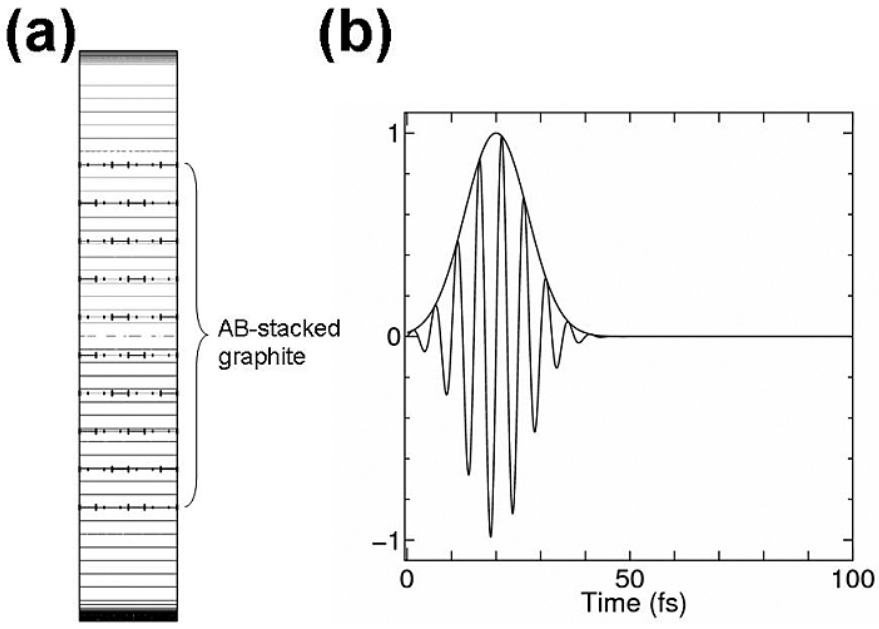

Fig. 1 (a) Contour lines of applied potential which gives electric field in normal direction to the graphite layers. (b)Time-dependence of the applied field shown in (a). The Gaussian envelope is also shown.

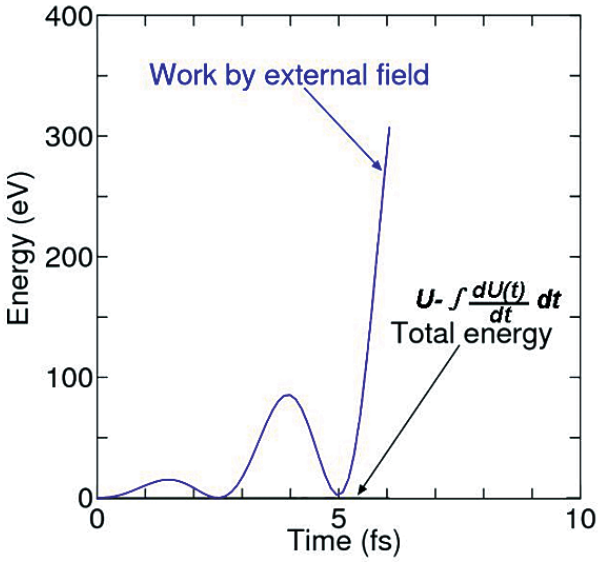

Fig. 2 Time evolution of internal energy of graphite shown in Fig. 1 (a) (blue line), and the same value extracted by integral of dU/dt, which is shown in an equation in the main text and corresponds to zero.

beam, and monitor induction of coherent phonon and structural deformation as well as electronic excitations. These phenomena will be useful for simulating non-thermal nano-fabrication process.

2.2 Generation of Mackay structure by using GSW rearrangements

The aim of the research is to investigate whether a certain nano carbon structure (including fullerenes and carbon nanotubes) is transformed to an objective structure by using only some sequential GSW rearrangements. Especially, this research can be applied to the process generating a "Mackay structure". It is expected that the Mackay structure is very stable and rigid, because it has three-dimensional high-symmetric property. For this reason, many researchers have been interested in the structure, and have analyzed its characteristics by the computer simulation. However, the process to generate the Mackay structure has not been clear yet.

It is known that a Mackay structure can consist of various numbers of the atoms. We have already found out the sequential process (it is named `path') for two Mackay structure consisting of 48 and 144 atoms. The larger the number of atoms, the more difficult we find the path. In this report, the path of a Mackay structure consisting of 192 atoms is found out newly. Figure 3 illustrates snapshots of the structure (192 atom times 8 primitive cells). The isomerization is realized by 232 GSW steps. The initial structure is 4-connected CNT shown in Fig. 3 (upper figure). The 4- connected CNT is also used as initial structure of other small Mackay structures, but the connecting position is different. We guess that the initial structure of larger size Mackay

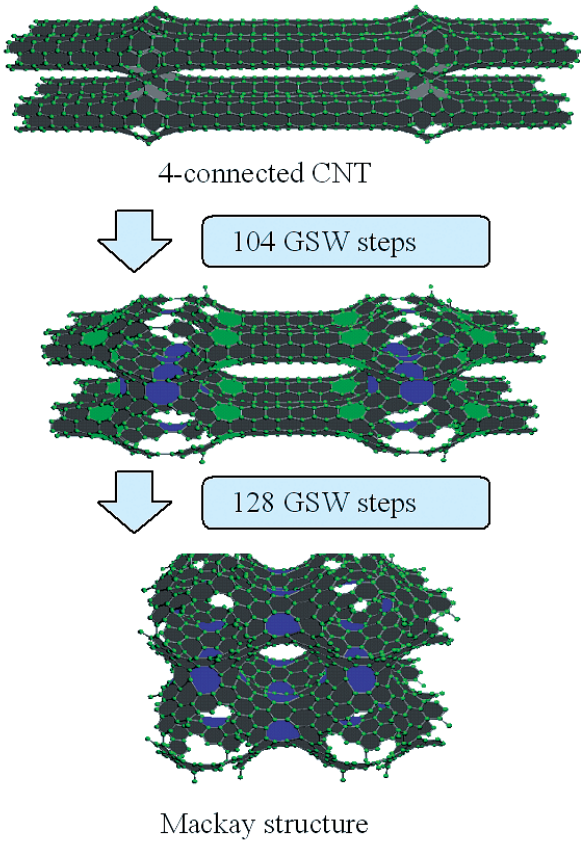

Fig. 3 Snapshot of path (192 atoms times 8 primitive cells).

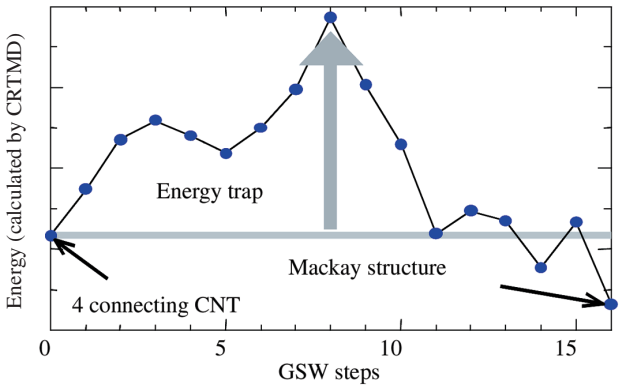

Fig. 4 Energy of each structure.

structure is also (8,8) 4-connecting CNT, but that the connecting position is different.

Next, we focus on the energy of the structure. The energy of each structure was calculated by using Huckel method. However, this method is not sufficient for calculating the energy of the system. Thus, we adopted the CRTMD instead of Huckel mehod. This report deals with the structure consisting of 48 atoms, because it is difficult to calculate the structure consisting of the large number of atoms. The energy of each structure is shown in Fig. 4. Although there is energy barrier in the path, the barrier is not so high. Furthermore, the energy of the Mackay structure is lower than that of initial structure. These results confirm that there

is the possibility of the realization of the Mackay structure.

The energy of paths of other Mackay structures (144 and 192 atoms) will be calculated by using CRTMD. We will investigate the possibility of realization of the Mackay structure.

2.3 Hydrogen adsorption on Transition-metal -decorated Carbon Nanotube

Global warming and abnormal weather caused by exhausted gas by fossil fuel are serious environmental problems in the world. Efforts to reduce carbon dioxide gas are required for environmental protections. In this context the clean energy system such as hydrogen fuel is at a human's desire. But it would highly cost us enormously under the necessity of sustaining high pressure or low temperature to hold it in a tank because of strong quantum effect of hydrogen atom. From safety points it is still under the way to use such type of fuel for practical application.

The success of hydrogen storage technologies critically depends upon discoveries of novel materials that could store and extract large amounts of hydrogen under economical and ambient conditions. Finding new materials of storing large amount of hydrogen at ambient temperature and relatively low pressures with small volume is crucial for hydrogen fuel storage.

We approached to the hydrogen storage by means of CNT through the first principle molecular dynamics. The hydrogen adsorption ability on a single Ti covering the surface of CNT has been reported in papers. However the researchers are based on an assumption that Ti atoms have never been segregated on the surface of CNT. The interaction between Ti atoms is not taken into account in the discussion about the Hydrogen storage.

We have carried out a large-scale simulation for hydrogen and Ti atoms dynamics considering the direct interaction between Ti atoms on CNT. Our simulation revealed that if many Ti atoms taken account of Ti-Ti interaction are introduced on the surface of a CNT, Ti atoms tends to form a Ti cluster by strong bonding force. As for Hydrogen adsorption, some hydrogen molecules are dissociated into individual hydrogen due to a strong chemical adsorption effect inside the Ti cluster shown in Fig. 5. Such an interaction between Ti atoms changes the properties of Hydrogen adsorption. The segregation of Ti atoms reduces the weight percent of storing hydrogen molecule. Finding more advantaged transition metal for hydrogen adsorption, we also investigated the properties of another transition metals in terms of the binding energy between transition metals and the state of hydrogen adsorption. It is concluded that hydrogen storage materials be able to be synthesized from the first principle molecular dynamics.

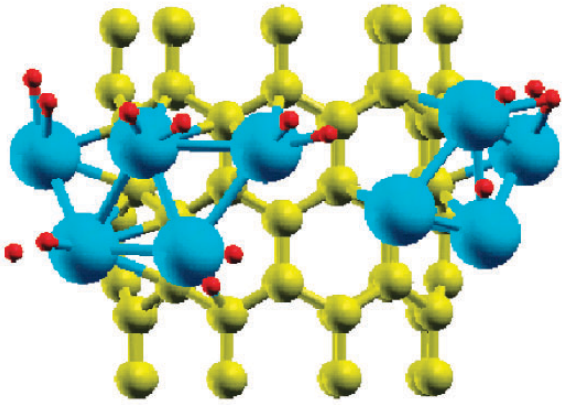

Fig. 5 Hydrogen adsorption for CNT. Hydrogen atoms and molecules are chemically and physically adsorbed on Ti cluster, respectively.

2.4 Growth Mechanism of CNT

Controlling growth process of CNT on metallic catalysts is an essential requirement to provide pure crystalline CNT for electrical applications as device and wire. There has been large progress in the experimental production of CWNTs. Nevertheless, the growth mechanism of pure CNT is still poorly understood.

As for theoretical calculation, classical molecular dynamics simulations based on empirical potential were mainly used to study the behavior of metallic Fe nano-particle catalyst and growth of CNT in chemical vapor deposition (CVD). The calculated CNT structures are not complete with large number of defects. The results gave rough explanation for the growth mechanism of CNT and the empirical potential using simulation is under development.

We have carried out the investigation on growth of CNT

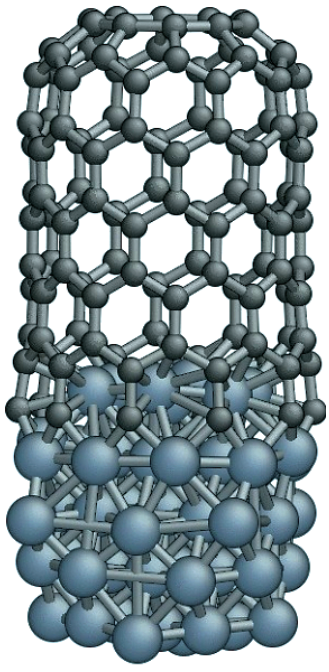

Fig. 6 Structure of interface between Fe cluster and CNT.

from first principle MD method. Firstly the conformity of CNT structure with Fe catalyst cluster was calculated. Iron catalyst cluster of 55 atoms with γ-phase (FCC) contacting the up-growth CNT was choose for the initial structure to start MD. In the simulation, we revealed that nano interface between Fe cluster and CNT is energetically stable as shown in Fig. 6. The results suggest that if the provided carbon atoms are flying to Fe surface, the provided carbon atoms are able to jump into CNT for the growth by advantage of the interface. As the next stage we will consider behavior of the provided carbon through simulation.

2.5 hole-doped diamond superconductor

We have been evaluating the superconductivity of novel materials on the basis of a new superconducting mechanism that the interaction between electrons changes from repulsive to attractive through the charge density fluctuation induced by the lattice vibration.

In the current year, we have developed further this superconducting mechanism, taking into account the time dependence of the bare Coulomb interaction between electrons. As an application, we investigated that at what temperature ideally hole-doped diamond becomes superconducting. For quantitative analyses using our scheme, it is inevitable to perform large-scale tight-binding molecular dynamics simulation consisting of at least several thousand atoms; therefore we executed our scheme on the Earth Simulator. Our code has been highly tuned to perform calculation on the Earth Simulator. The sustained performance of 4.82 Tera flops was achieved for the simulation with 8192 carbon atoms by using 256 nodes (2048 PEs) of the Earth Simulator. The resulting computing efficiency is 60.2% of the peak performance. To estimate T_c for a given hole concentration, the simulation took about 8 hours of computing time.

Our result shown in Fig. 7(b) indicates that pure diamond with 0.03 holes per atom is possibly the superconductor with 75 K. On the other hand, the T_c's observed in experiments are lower than those estimated by simulation. Recent precise measurements, however, show that synthesized samples incorporate hydrogen atoms. Under such circumstances, further theoretical and experimental studies will resolve the discrepancy.

As seen from Fig. 7, the value of T_c's are rather sensitive to the used approximation; therefore in order to improve our simulation, it is necessary to incorporate the other neglected effects listed below:

(1) Charge fluctuation by the non-linear response to the lattice vibration,

(2) Off diagonal elements with respect to orbital of effective interaction between electrons,

(3) Use of the renormalized Green's function in the self-energy.

Henceforth we will take into account these effects.

Our simulation method has marked an important first step toward estimating T_c's of various superconductors with high accuracy far beyond the limitation of the previous methods.

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, Applied Physics Letters, "Ultrafast reconstruction of graphite by irradiating with highly charged ions", Vol.91, p113120 (2007).

[2] Y. Miyamoto, "Deformation of sp2 Graphitic Nanostructure by Irradiation with Highly Charged Ion", APS March Meeting (2007).

[3] S. Nakamura, "A New Method for Calculating the Dielectric Response Function - Application to hole-doped diamond superconductors -", International Symposium on Frontiers in Computation Science of Nanoscale Transport (Poster Session), Tokyo University of Science, Tokyo,

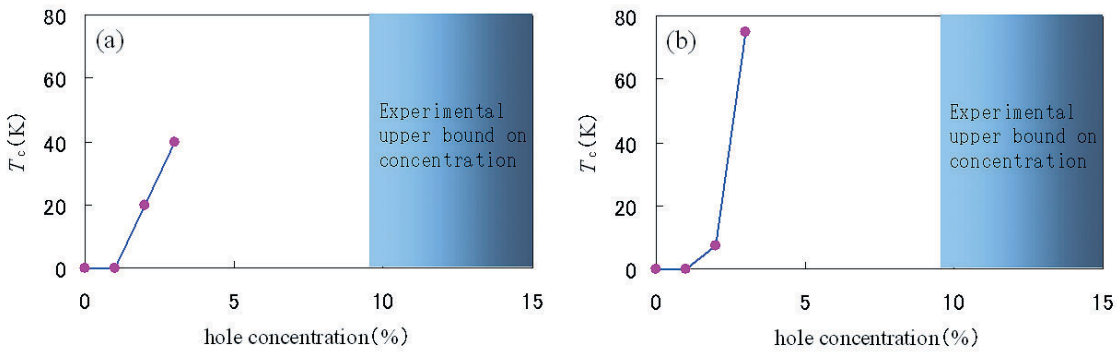

Fig. 7 T_c versus hole concentration in case of (a) neglecting the time dependence of the bare Coulomb interaction, (b) incorporating the time dependence of the bare Coulomb interaction.

June, 2007.

[4] S. Nakamura, S. Tejima, D. Tomanek, and H. Nakamura, "New Large Scale Simulation for Evaluating Superconductivity", SC2007, HPCNano07 workshop, Reno-Sparks Convention Center, Reno, NV, November, 2007.

[5] Y. Miyamoto, Electron-Ion Dynamics throughout Collision of Highly-Charged Ar on Stacked Graphite and Subsequent Structural Change, Third Symposium on Computational Challenges and Tools for Nanotubes (CCTN07), Rio de Janeiro, Brazil, June 22, 2007.

[6] S. Tejima, Large Scale Density functional simulation of Hydrogen adsorption on Carbon, Third Symposium on Computational Challenges and Tools for Nanotubes (CCTN07), Rio de Janeiro, Brazil, June 22, 2007.

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　　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，藤沢　義和*3，中村　　壽*1

*1　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　本田技術研究所

1. 研究目的

優れた物性を予想される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・H18 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結果を以下に示す。(1)ナノ構造加工の面について、時間依存密度汎関数理論(TDDFT)を用いて、物質に時間変調する電場を印加した際の電子とイオンのダイナミクスを計算する機能を、従来から地球シミュレータにてしていた計算コードに追加し、この機能により、摂動理論では表現できない強力なパルス光に対する物質の応答を計算することを可能にした。多層グラファイトにパルスレーザーを照射した状況におけるエネルギー吸収のシミュレーションにおいて、この計算プログラムによる計算の数値精度の安定性が保たれていることを示し、数値計算の精度と安定性を保障する条件がシミュレーションを行っている最中に保たれるエネルギー保存則であることを見出せたこの手法により、フェムト秒レーザーを照射したナノ炭素材料において、コヒーレントフォノンや構造変化、電子励起の出来る様子をシミュレートし熱に頼らない新たな加工方法をシミュレーションで探ることが可能となった。(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比較的小さなマッカイ構造の生成過程を対象として検討を行ったが、本年度はコードの高速化しより大きなマッカイ構造の生成過程を明らかにした。その結果、大きさの異なるマッカイ構造であっても初期構造はその接続位置のみ異なる(8,8)CNTより生成できることが推測された。また、昨年度まではHuckel近似による構造エネルギーを計算していたが、本年度はより正確に構造エネルギーを計算するためタイトバインディング法(CRTMDコード)を用いた。その結果、生成過程中にエネルギーバリアがあるが、初期構造よりもマッカイ構造のほうがエネルギーが低くなっていることから、生成の可能性があることをエネルギーの面からも明らかにした。(3)ナノチューブ応用として、ナノチューブに吸着した単一チタンが水素吸蔵体となるこが報告されているが、より現実的に多数チタンを考慮した水素吸着体の性質を明らかにした。従来の結果とは異なり、チタンはCNT上で凝縮しクラスターを作り、水素は原子としてチタンクラスターに化学吸着する現象が起こることを示した。チタンに加え、全遷移金属についてクラスター化の生成についての知見を得え、最適水素吸着体の探索に取りかかることができた。(4)デバイス応用の面から、CNT生成メカニズムが明らかにすることにより、量子ワイヤー等に用いる欠陥のない長尺CNTを生産する技術の確立を目指した。CVD法において鉄クラスターを核にしてCNTが成長するメカニズムの理解の予備計算として、鉄クラスターとCNTの界面がエネルギー的に安定に存在することを示した。鉄クラスターが気相から炭素を取り込に、この安定な界面を利用してCNTに炭素を供給することが可能であることが明らかになった。(5)超伝導転移温度(T_C)を上げるための研究が盛んになってきているホウ素ドープダイヤモンドを対象に、昨年度は現実的なホール濃度でのT_Cのシミュレーションを行った。その結果、電子相関が十分に考慮されていないことが明らかになったため、本年度は電子相関をさらに正確に取り入れた超伝導シミュレーションの研究開発を推し進め、より高い精度のT_Cを得ることに成功した。また我々の開発した新手法は、従来の手法の限界を遥かに超えた超伝導シミュレーションの実現への道を切り開くものである。

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, 時間依存密度汎関数法, カーボンナノチューブ, 水素吸蔵体, ナノダイヤモンド