

# NIMS

*2010. January*

# NOW

**International**

**Diamond Research  
at NIMS**

**From Gem to Material**





## A New Year's Message from the President

Prof. Sukekatsu Ushioda  
President of NIMS



NIMS has accumulated many significant achievements in the last 10 years as an R&D-type Independent Administrative Institution (IAI) specializing in materials research. As we begin the New Year, we are determined to devote even greater effort for advances in the R&D of materials.

With the start of Japan's 4th Science and Technology Basic Plan, our government is redirecting science and technology policy toward so-called "outcome-oriented" strategies. Today we face many urgent global and social issues requiring solutions, including environment and energy-related problems and the problems of inadequate food and water supplies. The idea behind the outcome-oriented strategy is to define these issues clearly and to direct the R&D effort to solve them with high priority. The new policy has been reached as a result of recognizing the importance of research and development for the society now and for the future of humankind. We intend to carry out our research and development in line with the government policies.

One effort in this direction is the establishment of the "Innovative Center of Nanomaterials Science for Environment and Energy." The Center was created in response to the "Program for Development of Environmental Technology Using Nanotechnology" promoted by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). NIMS was chosen to host the Center, which has established four target areas (photovoltaic cells, photocatalysts, rechargeable batteries, and fuel cells) aimed at solving energy and environmental problems. We are assembling a "Dream Team" of frontline experts from industry, universities, and IAI's to carry out extensive basic and generic research to solve these problems. By investing large efforts in this Center, we hope to make a significant contribution to Japan's announced national goal of reducing CO<sub>2</sub> by 25% by 2020.

A second effort is the World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), which was established at NIMS two years ago. It has already earned an excellent reputation for promoting internationaliza-

tion, as exemplified by the recruitment of eminent foreign researchers, a high ratio of foreign researchers over 50%, and the use of English as a common language. MANA also continues to produce outstanding results by promoting exploratory work to establish new directions in nanotechnology. At the same time MANA is accumulating research results that should blossom into broad applications in the near future, such as nanosheets, an atomic switch, photocatalysts, etc. MANA aims at becoming one of the world's prominent research centers within 10 years by creating innovative materials important for a sustainable 21st century society.

In the area of internationalization, we now require a large number of our staff to participate in language training to improve the English proficiency. For the same purpose we will initiate a program to encourage our young staff to spend extended periods in our affiliated laboratories abroad. We hope to maintain approximately 10% of tenured researchers in those laboratories. Working and living overseas is extremely effective in letting researchers mature in the international setting. In addition the friendship formed overseas can serve as an inducement for talented foreign scientists to join NIMS. Young researchers in particular should go overseas with strong ambition. If, as a result, NIMS becomes a "supply source" for outstanding scientists, that will be good for Japan, and we should be pleased.

For Japan to be respected as a leading nation, it is essential that we contribute to solving global-scale problems by maintaining our superiority in basic science and industrial technology. From this viewpoint I believe that the most important mission for NIMS is to maintain the superiority of Japan's technology through development of innovative materials.

We wish to carry out our daily work with joy with the ideal, "Think-for-yourself and do-it-for-yourself." As we begin 2010 we request your unchanging guidance and support. We hope that you will all have a very happy and rewarding New Year.

## Special Feature

# Diamond Research at NIMS

## Elucidation of the Excellent Properties of Diamonds and Their Application to Innovative Materials



### From Gem to Material

NIMS Honorary Advisor Mutsukazu Kamo

Diamond is a substance which is familiar to everyone as the "king of gems." However, as progress in science and technology has made it possible to elucidate the various properties of diamonds as a substance, diamonds became a focus of interest as a material.

Diamonds are used in a wide range of applications, for example, in tool materials, which take advantage of their nature as a superhard substance, in electronic materials as a wide bandgap semiconductor with high thermal conductivity, and in biomedical materials as a substance with good biocompatibility. In recent years, it has also been found that diamonds possess superconductivity, and research on application to quantum computers has begun.

Expansion of these application is greatly due to the development of chemical vapor deposition (CVD), the simplified synthesis method for diamond.

Since the discovery that diamonds are form of carbon, many researchers have taken on the challenge of artificial synthesis. The first successful synthesis of diamonds was achieved by companies in Europe and the United States in the 1950s. The key point was the development of devices capable of generating high pressure. In Japan, the National Institute for Research in Inorganic Materials (NIRIM; a predecessor of NIMS) began research on high pressure synthesis in the 1970s. This work placed enormous expectations on research and development of technologies for generating high pressure.

### Start of Diamond Research

Diamond research at NIMS began with a high temperature, high pressure method developed by the Carbon Group at NIRIM, which started in 1969. The Carbon Group was reorganized as the Diamond Research Group in 1974. Although work centered on the high temperature, high pressure method, the group also investigated the shock compression method and CVD method as exploratory research topics.

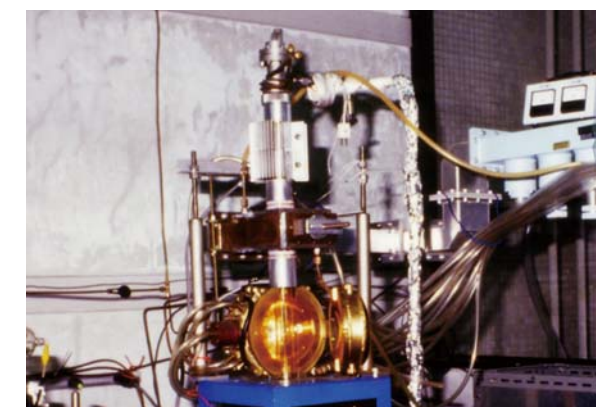
In work on the CVD method, over the 5 year period up to 1979, the group conducted research on surface adsorption of carbon materials by the thermal desorption process, graphitization of diamonds by oxygen, diamond growth from a vapor phase using isotopes of carbon, and evaluation of various carbon materials using Raman spectroscopy. All of these basic research have linked to CVD of diamonds.

research on the CVD continued as exploratory research.

The 1981 edition of the Proceedings of the International Conference on Crystal Growth, which had been held in Moscow the previous year, reported startling results in connection with CVD of diamonds by Spitsyn et al., including photographs of diamond particles deposited on heterogeneous substrates such as silicon and copper, and dependency of the crystal plane on the synthesis temperature.

The attention of one member of our

research group was drawn to the description of atomic hydrogen in that report. This researcher activated hydrogen by heating it to nearly 2000°C, and thereby succeeded in CVD of diamonds by the hot filament method. Although research on this process had begun 7 years earlier, this at last raised the curtain on CVD techniques using gas flow-type devices. Following this success, in 1982, we also succeeded in synthesizing diamonds by a microwave plasma method and a high frequency plasma method.



Microwave plasma method device for synthesizing diamonds develops in NIRIM.

### Success in CVD

In the second-period research, which began in 1979, work centered on synthesis of sintered bodies by the high temperature, high pressure method, and

In comparison with natural diamonds and diamonds synthesized by the high temperature, high pressure method, the diamonds which were synthesized by the CVD method were considerably inferior in optical properties, reflecting the relatively impurity and crystallinity of the materials. However, following improvements in the synthesis conditions, measurement of exciton emission by cathode luminescence and other results confirmed that vapor-deposited diamonds are by no means inferior to natural diamonds or high temperature, high pressure diamonds.

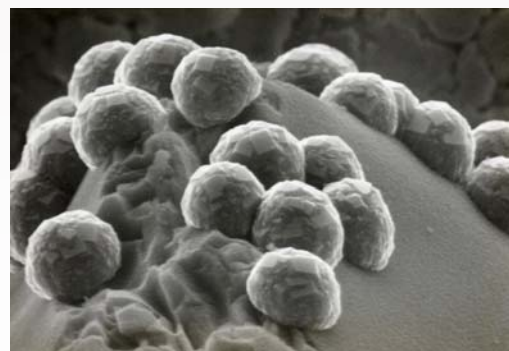
### Expectations for Future Applications

After the successful synthesis of diamonds by NIRIM, diamond research in Japan increased rapidly. In particular, a succession of new techniques were devel-

oped, including electron-assisted chemical vapor deposition (EACVD), methods using a combustion flame, direct-current plasma methods, and thermal plasma methods, among others. Although these various methods have been developed, microwave plasma methods have now become the main stream from the viewpoints of controllability and workability.

The market for vapor-deposited diamonds is not large. However, the practical applications realized to date include cutting tools, speaker diaphragms, wear-resistant sliding parts, heat-spreader, and surface acoustic wave filters. In 1996, we have also made it possible to

synthesize n-type semiconductors, which do not exist in nature, and development of devices using their electrical properties is expected.



The first diamond particle synthesized by microwave plasma method.

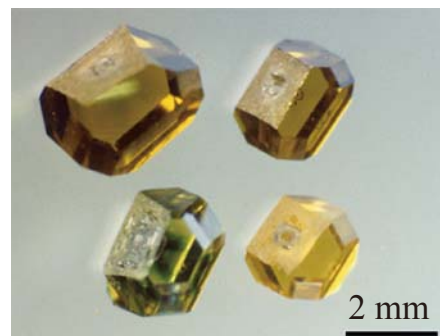
## A Variety of High Pressure Synthetic Diamonds

Hisao Kanda, Tsukuba EXPO'85 Memorial Foundation / NIMS Sensor Materials Center Research Advisor

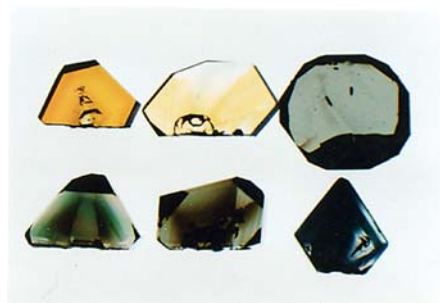
High pressure synthetic diamonds show polycrystalline form and single crystal one. Usually polycrystalline diamond is made with sintering diamond powder using metallic catalyst such as cobalt as an additive. NIMS has developed another type of sintered diamond using nonmetallic catalysts such as carbonate, etc, based on discovery that such nonmetallic materials have catalytic effect on transformation of graphite to diamond. Because this type of diamond has excellent wear resistance, expectations that this material show high performance as cutting tools are high. Recently, researchers at Ehime University synthesized transparent polycrystalline diamonds by direct transformation of graphite. Thus, research on polycrystalline diamonds is continuing to evolve.

In the field of single crystal diamonds, a company in Europe synthesized a large-scale crystal with a maximum weight of 35 carats (diameter: 2 cm), and carat-sized crystals available for use as gems have also appeared in the market recently. At NIMS, one focus of research is control of impurities.

Although nitrogen and boron are known to be readily incorporated into diamond lattice, it has been found that metallic elements such as nickel and cobalt are also incorporated to produce specific color and luminescence (see photos). Recently, Russian researchers synthesized superconducting diamonds by doping with high concentrations of boron. The appearance of other diamonds with new properties is also expected in the future.



High pressure synthetic diamonds. The yellow and green colors are attributable to nitrogen and nickel impurities, respectively.



Cross section of high pressure synthetic diamonds. The yellow color is attributable to nitrogen impurities, brown and green are attributable to nickel, and blue is attributable to boron. The colorless stone at the upper right contains undetectable impurities.

## Diamond Semiconductors and Deep UV Sensors

Yasuo Koide (Group Leader), Optical Sensor Group, Sensor Materials Center

### Diamonds and Electronics

Since 1982, the development of diamonds in the field of electronics has progressed steadily through the establishment of thin film growth techniques for high quality single crystals, establishment of p-type and n-type electrical conductivity control methods, and physical understanding of the diamond surface and metal and insulator/diamond interfaces. The author is one of the researchers who has been continuously involved in this field since first participating in the development of p-type diamond low resistance ohmic electrode materials, and is currently engaged in the integrated research from crystal growth of diamond thin films to device development.

Here, I would like to introduce the physical properties of semiconductor devices in which diamonds are a distinctive feature, while comparing experience obtained through the Si-ULSI (ultra-large scale integrated circuits) process, GaAs integrated circuit process, and GaN light-emitting device process.

### Deep-Dopant Effect

Diamonds have a bandgap of 5.5eV at room temperature, and have an indirect bandgap structure comprising a multi-valley structure like that of silicon. Because diamonds are covalent bonding wide gap semiconductors which do not have ionic bonding property, their permittivity (dielectric constant) is relatively small, being less than half that of other Si and III-V group compound semiconductors. According to the effective-mass model of solid-state physics, it can be predicted that the ionization energy (impurity state) of n-type and p-type dopants will be larger in lower permittivity substances. Experiments have also shown that the ionization energy of the dopants is large. For this reason, it is not easy to obtain an adequate electron and hole concentrations to operate a semiconductor device at room temperature. In actuality, it is a distinct feature of diamonds that the electrons and holes in diamonds are easily compensated by residual impurities (carrier extinction), and spatial diffusion of the electrons and

holes occurs easily. "Deep-dopant effect" is defined to be a terminology for the diverse electrical/optical properties which appear with the large ionization energy of dopant donors and acceptors as a distinct feature. Although this has drawbacks in comparison with other semiconductors, in sensing of deep ultraviolet rays (DUV; wavelength: 190-280nm, see Fig. 1) using diamonds, it was found that sensor sensitivity is dramatically improved due to the appearance of an extremely large photoconductive gain phenomenon, which is attributable to this deep-dopant effect.

### Development of UV Sensor

Taking advantage of this important feature, a "Solar-Blind UV Sensor" was successfully developed. This device detects only deep ultraviolet radiation, even during daytime in the presence of sunlight, has extremely good thermal stability and high sensitivity, and uses low voltage drive. The world's first fire detection system using a diamond deep ultraviolet sensor was also successfully developed, as shown in Fig. 2.

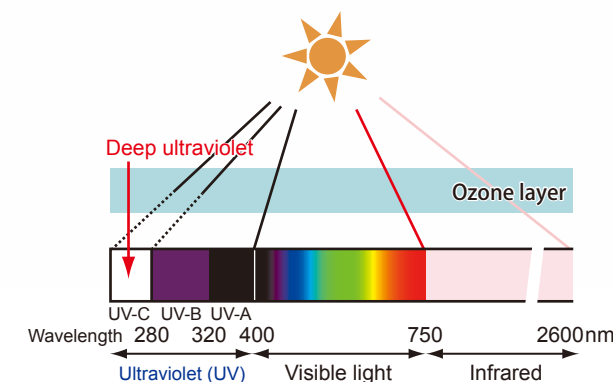


Fig. 1 Spectrum of sunlight at earth's surface and explanation of deep ultraviolet sensor.



Fig. 2 Fire detection system using diamond solar-blind UV sensor.

## Diamond Thin Film Growth and pn Junction Device

Satoshi Koizumi, Optical Sensor Group, Sensor Materials Center

### Research on Synthesis of n-type Diamonds

The fact that it was possible to grow diamonds by the chemical vapor deposition (CVD) method was an epoch-making advance. In explaining the importance of the CVD process, although thin film growth had been difficult with high pressure synthesis, this is comparatively easy by the CVD process, offering the new possibilities of hard coating and positive application to electronic devices. Utilizing the CVD process developed by its predecessor, the National Institute for Research in Inorganic Metals (NIRIM), NIMS is actively engaged in research on the growth of high quality semiconductor diamonds, and in particular, on synthesis of n-type diamonds, which do not exist in the natural world.

### Success in Formation of pn Junction

In experiments on synthesis of n-type diamonds, it was discovered for the first time that the {111} crystal surface, which had attracted little interest in the past, is suitable for doping with electrically

active phosphorus atoms. The successful synthesis of an n-type diamond, which was convincingly announced in a paper in 1997, attracted great attention as an indispensable technique for realizing diamond electronic devices. The special synthesis conditions which were found for realizing high quality in growth of the {111} crystal plane, in which crystal defect is usual, were deeply related to this success. Although the obtained n-type diamond also has problems, namely, high resistance and large activation energy of the phosphorus used as a donor, this is a special diamond which enables electrical conduction by electrons. Utilizing this property, we succeeded in formation of a pn junction. Here, recombination light emission was observed when electrons from the n-type diamond and holes from the p-type diamond were mutually injected through the junction interface. The wavelength was 235nm (5.27eV), which is the same as the characteristic free-exciton recombination emission in diamonds. When the paper was published in 2001, this was the shortest UV wavelength (highest energy) which could be obtained from light-emitting diodes.

### Deep Ultraviolet Sensor for Detection of UV Radiation

At present, this research is continuing as joint research with the Energy Technology Research Institute (ETRI) of the National Institute of Advanced Industrial Science and Technology (AIST). Up to 100  $\mu$ W has been achieved as 235nm deep ultraviolet output with a pin device (device in which a light emitting layer of high purity diamond is sandwiched by a pn junction). **Fig. 1** shows the light emission of the LED which we first reported (above) and a recent LED (below). Unfortunately, the light which can be seen in the photograph is the visible light emitted due to crystalline defects, and the key UV portion cannot be reproduced. However, in the recent LED, we obtained deep ultraviolet light emission with an integrated intensity stronger than the visible light region. If the process of light emission by the pn junction is reversed, the device functions as a light sensor or photoelectric conversion device

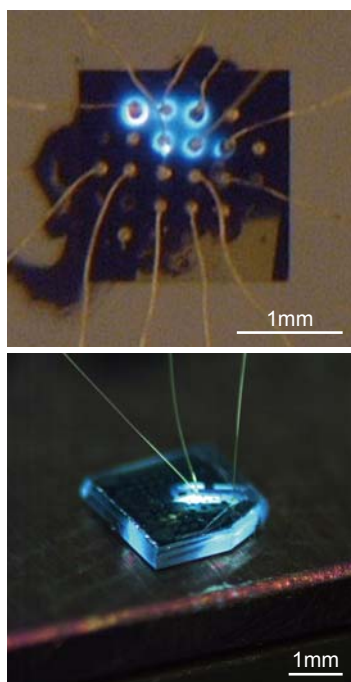


Fig. 1 Light emissions by the LED initially reported (above) and a recent LED (below).

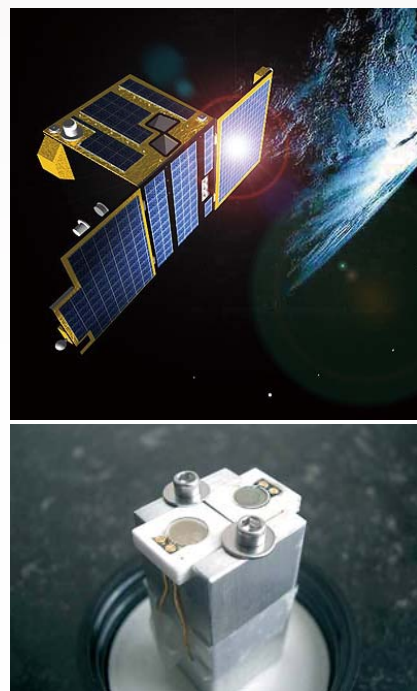


Fig. 2 PROBA-2 solar observation satellite (above) equipped with the NIMS sensor chip (below).

which converts light to electricity. Due to the wide band gap of diamond (5.47eV), we could see good operation as a deep ultraviolet sensor capable of detecting UV radiation with wavelengths shorter than 225nm.

### Application in Solar Observation Satellite

A sensor chip using diamond material in the pin device, in the same manner as with the above-mentioned LED, was fabricated on the surface of a large 5mm disk-shaped diamond substrate. Based on a high evaluation of its excellent stability, the sensor was adopted in a project of the European Space Agency (ESA). **Fig. 2** shows a view of the sensor chip and the PROBA-2 solar observation satellite in which it was installed. In parallel with these studies, we are continuing research toward the future application of pn junction devices in electronic emitters, power devices, and the other equipments. The ultimate diamond device is considered to be an advance beyond the semiconductor devices which have developed through germanium, silicon, SiC, and GaN.

## Development of Diamond Schottky Diode

Tokuyuki Teraji, Optical Sensor Group, Sensor Materials Center

### Diamond Diodes Contributing to Energy Saving

The share of electric power in primary energy is increasing, and in addition to conventional large-scale power generation, the distributed power generation systems are increasingly introduced. In this situation, the development of small-scale power control devices with high conversion efficiency for distributed power generation is desired. As one distinctive feature of diamonds, the dielectric breakdown field is extremely high, being 30 times that of Si and 3 times that of SiC. Thus, if diodes can be produced using diamond materials, it will be possible to realize simultaneously miniaturization of the device and reduced power consumption. The thermal conductivity of diamonds is the largest among the semiconductor materials, which means that the diamond material itself can function as a heat sink for the heat generated during operation. Furthermore, because diamonds are a wide band gap semiconductor, with a band gap equivalent to 5 times that of Si, high temperature operation and the potential to control large currents are distinctive features of diamond diodes. Thus, high expectations are placed on the development of ultra-low loss power diodes using a diamond substrate as research contributing to energy saving and protection of

the global environment.

### Development of a Diamond Schottky

A diamond Schottky diode was fabricated employing a newly-developed surface treatment method using vacuum UV and ozone. Good results were obtained in an evaluation of the properties of the diode (**Fig. 1**), which showed a withstand voltage of more than 1kV and a reverse leakage current of less than 30pA ( $\sim 10^{-7}A/cm^2$ ).

### Stable Properties at High Temperature

As operating characteristics (**Fig. 2**), it was found that the device operates satisfactorily in a wide range of temperatures from  $-120^\circ C$  to  $300^\circ C$ , showing no deterioration of properties over this temperature range. Development of SiC Schottky diodes is progressing, and stable operation has been reported at temperatures up to  $250^\circ C$ . In contrast, however, the prototype diode fabricated in this research shows high stability even at  $300^\circ C$ , in spite of having a simple structure in which the metal is merely vapor deposited to the diamond substrate. It is thought that even more excellent high temperature operating characteristics can be obtained in the future by improving the

device structure. From **Fig. 2**, it can be understood that the forward-direction saturation current density (e.g., voltage 3V) is larger at  $300^\circ C$  than at room temperature. In previously-researched materials, including SiC, the saturation current density decreases as the temperature increases; in other words, resistance during operation of the device increases. The main cause of this increase in the saturation density is a decrease in carrier mobility in crystal. However, in diamonds, carrier concentration continues to increase in this high temperature region, and as a result, resistivity shows its smallest value at around  $300^\circ C$ . Based on this as well, it can be said that the diamond Schottky diode has excellent high temperature operating characteristics at around  $300^\circ C$ .

### Further Improvement of High Temperature Stability

When the temperature of the diode was increased to  $600^\circ C$ , diode properties were satisfactory, but a change was observed. This change was not a problem attributable to the diamond itself, but is understood to be caused by the degradation of the interface between the electrode metal and the diamond. Thus, it is thought that further improvement in the high temperature stability of the diode can be achieved by establishing an interface forming method which secures high thermal stability.

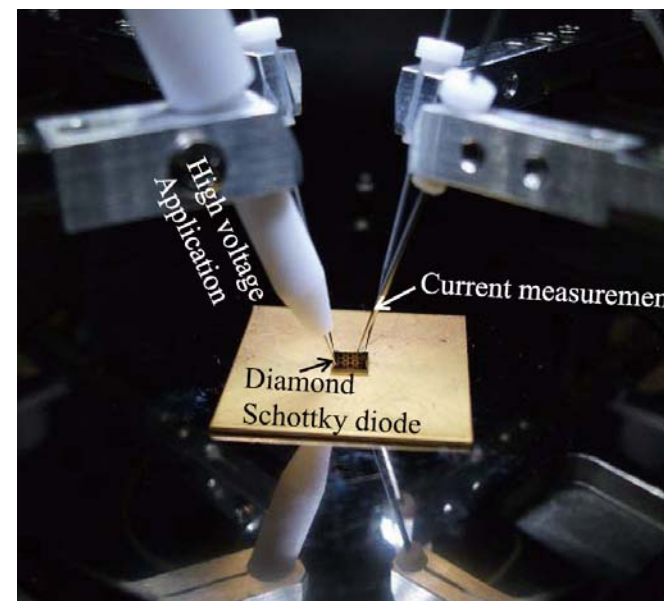


Fig. 1 Evaluation of diode characteristics.

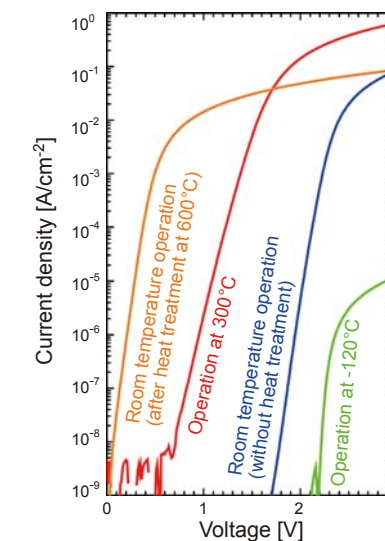


Fig. 2 Operating characteristics

## Superconductivity in Diamonds

Yoshihiko Takano (Group Leader), Nano Frontier Materials Group, Superconducting Materials Center

### Preface

Pure diamonds are harder than any other substance, transparent and beautiful, and have high heat conductivity. However, diamonds are also an insulator which does not pass electricity. Many people would be surprised to learn that there is a diamond which displays electrical conductivity like a metal. Even more astonishing, at low temperature, this diamond shows absolutely no electrical resistance; in other words, it passes a current in a superconducting state. In fact, it is possible to synthesize this mysterious kind of diamond.

### Boron Changes the Properties of Diamonds

Diamonds are formed by covalent bonding of carbon atoms. Beautiful natural diamond gemstones appear at a glance to be pure, but in fact, they contain impurities such as boron and nitrogen. Considering this, what kind of diamond can be obtained by synthesis with an artificially high concentration of boron?

Because boron has one fewer electron than carbon, a one-electron deficient state can be obtained by substituting a boron atom for one of the carbon atoms forming the diamond. This is called an

"electron hole," or simply a "hole" (positive carrier). Fig. 1 shows the electrical resistivity of diamonds having various concentrations of boron. Diamonds with a low doping of boron display the characteristics of a semiconductor, but when the boron concentration exceeds  $3 \times 10^{20} \text{ cm}^{-3}$ , the diamond becomes a metal. When a diamond that displays the characteristics of a metal is cooled to a low temperature of around 10K, its electrical resistance suddenly decreases and a zero resistance state appears. This is referred to as the superconducting phase transition. When a substance achieves the superconducting state, electrical resistance is completely eliminated, and a current can flow with absolutely no loss.

### Development of Josephson Device

As mentioned above, the properties of diamonds can be controlled over a wide range, which includes behavior as an insulator, semiconductor, metal, and superconductor, simply by controlling the concentration of boron. Taking advantage of this feature, we developed a Josephson device using only diamond. Fig. 2 shows a schematic diagram of the fabricated

device. Using a single crystal diamond as the substrate, a thin film of superconducting diamond, an extremely thin semiconducting film, were formed in succession while controlling the concentration of boron. In the semiconductor layer, the boron concentration was adjusted to be below the metal-insulator transition concentration. A Josephson device is a fundamental device in superconductivity, corresponding to transistors in the field of semiconductors, and can be used in diverse applications, including magnetic flux sensors, voltage standards, superconducting computers, etc.

### A Novel Diamond Device

When producing LSIs and similar devices, different substances are generally used in the metal and insulator parts, and these materials have different properties. As a result, problems of compatibility and affinity may arise when the materials are stacked. In contrast, a device produced entirely from single crystal diamond, from the substrate to the thin film, would have extremely high compatibility. Furthermore, because diamonds are physically and chemically stable and display high thermal conductivity, it would be possible to produce the ideal device. From this viewpoint, we are developing novel devices which use the most of the advantages of diamonds.

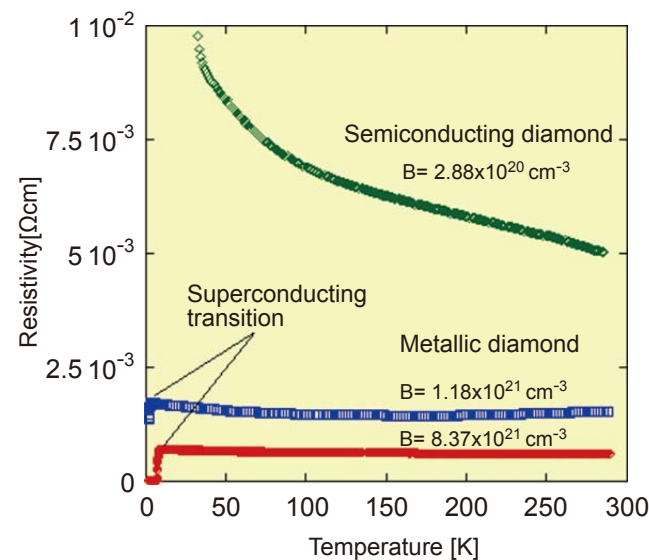


Fig. 1 Metal-insulator transition and superconducting transition of boron-doped diamond.

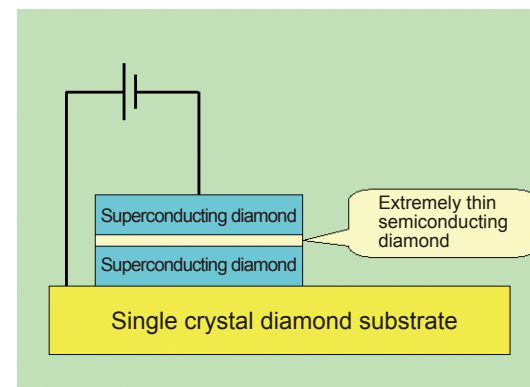


Fig. 2 Schematic diagram of Josephson device using only diamond.

Elected last year to a fellow of ASM International (American Society for Materials), Dr. Seiji Kuroda has more than 20 years of experience in the field of thermal spray coatings. Such coating technologies are widely used in areas such as large steel structures, production machines and engine parts. Dr. Kuroda's research has made a great contribution in elevating the coating process from an experience-based technique to a technology backed by science.



**Seiji Kuroda**  
Managing Director, Hybrid Materials Center

## Evolving Coating Technology from Know-How to Science

### Congratulations on becoming a fellow of the ASM.

Thank you. ASM International is a society for the science and engineering of materials based in the US. It was founded at the start in the 20th century as a forum for metal engineers. It was an honor for me to receive the award at their award ceremony in Pittsburgh.

### In graduate school you specialized in measurement.

My supervisor always told me that I should find for myself what objects I should measure, and introduced me to Prof. A. Hasui, the founder of the plasma spray laboratory at NRIM (National Research Institute for Metals, the predecessor of NIMS). When I visited the laboratory, I realized how powerful the process is and what a wide range of applications the research could have. Thermal spray is a technology of creating a relatively thick film over a matrix by bombarding it at high speeds with fine particles of melted or softened metals or other materials. The quality of the film varies depending on the conditions, and the factors affecting this relationship were unclear. There were neither an adequate method to measure the velocity and temperature of particles or film thickness during deposition, and I was asked to measure these variables. As this matched my interests, I joined the institute in 1985. During my earlier period at the lab, their technical jargon was very unfamiliar to me (almost Greek), and I found myself asking the most basic questions.

### Where are thermal spray coatings used?

For example, zinc thermal spray coating is used on steel structures under the paint to prevent corrosion. Turbine blades of jet engines have a ceramic coating to withstand high temperatures. Coating is widely employed in manufacturing facilities and power stations for raising the durability of various component and protecting them from harsh environments. It is also used in space equipment and biomaterials. The advantage of coating is that it is thicker than paint or other thin films made by plating or vapor deposition techniques, being several hundred  $\mu\text{m}$  thick, and hence usually more durable. On the other hand, a sprayed coating is basically a layer of particles stacked side by side, and is liable to include pores. One key point is to develop a process that eliminates the chance of connected pores. I see this award as a recognition of my efforts to create a method for studying the fundamentals of coating process, as well as to develop new processes.

### What materials are used for substrates and coatings?

The substrate material can be metals, plastics, ceramics, paper, or almost anything. Coating materials include metals,

ceramics, polymers, or any combination of these. The process temperatures of spray coating are also diverse - there is plasma spray using arc discharge at over ten thousand  $^{\circ}\text{C}$ , the method using gas flame, the method using electrical heaters to warm gases, and so on. Particles with small diameters do not thermally affect the substrate severely, while high particle velocities enable adherence at lower temperatures. Understanding this kind of fundamental phenomenon makes it possible to use materials that could not be used in the past.

### How did you perfect it to a science?

I invented a device for measuring the stresses acting on the substrate during coating formation, for the first time in the world. There is a close relationship between the stress applied and the ease of particle adherence or detachment. Once the mechanism had been worked out, it became possible to make predictions. Recently, I was told that an American venture firm set up in a university adopted my research results to develop an instrument and software for calculating the stresses in the coatings as well as the stress-strain characteristics. We also developed a tool for measuring the temperature and speed of sprayed particles in flight. Recent research has finally shedding light on the mechanism of adherence. One can cut off a piece of the film with an ion beam and observe it under an electron microscope at very high magnifications to see the variations in adherence depending on the portion of the matrix.

### What is your dream?

My dream is to establish a research center for integrated research and development in surface engineering. Coating is a technology with a wide variety of practical uses in a world of growing environmental concerns. It is a key technology for the materials used in harsh and demanding environments, such as space or nuclear power plants. Here in NIMS, with such a large number of experts in various fields related to coating, I believe that the potential and benefit of establishing such a core for research is huge.

### Do you have any message for young researchers?

When you are young, it can be interesting to take a leap into a field that is somewhat outside your own specialization. It is a good opportunity to carry out original research.

## Safe, Easy-to-Use Far UV Light Emitting Device

### — Practical Application of Hexagonal Boron Nitride —

Optoelectronics Group, Optronic Materials Center  
High Pressure Group, Exploratory Nanomaterials Research Laboratory / Optoelectronics Group, Optronic Materials Center<sup>†</sup>

At present, light sources in the far ultraviolet region (wavelength: 280-198nm) are widely used in decomposition treatment of environmental pollutants by photocatalysts and in UV sterilization in hospitals, food processing plants, and similar applications. However, a large power supply device is necessary in conventional discharge lamp light sources, such as mercury lamps, and because the lamps contain mercury and other harmful substances, special care is required in their use and disposal. Thus, these systems have the drawback of being extremely difficult to handle.

In 2004, we discovered that hexagonal boron nitride (h-BN) displays highly efficient far UV light emission characteristics and began development of a safe UV light-emitting device using h-BN in the light source. Because h-BN is chemically and thermally stable, it is generally used in heat resistance and insulating materials. It has also long been known as a nontoxic substance. However, until our discovery in 2004, its light-emitting properties in the far UV region had not been clarified.

In the present research, the authors and the Research & Development Center of Futaba Corporation succeeded for the first time in the world in trial-manufacturing a flat-type monochrome far UV light-emitting device having a stable output of 0.2mW, which is a practical level. The basic principle of this device is the same as that of an FED (field emitter display). An electron beam from a field emission-type electron source is accelerated at high voltage, and excites the

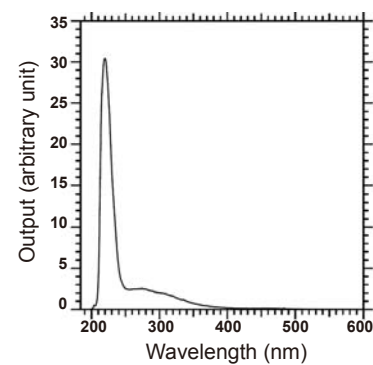
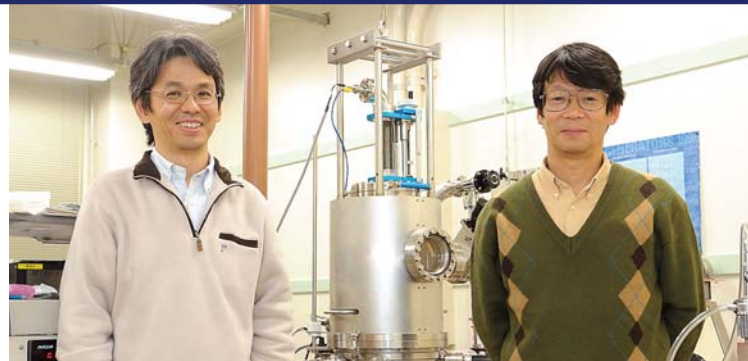


Fig.1 Output spectrum, comprising a strong UV component around 220nm and a weak adjacent region (250-400nm).



Kenji Watanabe

High Pressure Group Leader  
Takashi Taniguchi<sup>†</sup>

h-BN single crystal particles, which are the far UV phosphor, causing the particles to emit light. Virtually all of the light output has a wavelength component around 220nm. The device does not output infrared, which is a cause of heat (Fig. 1). Furthermore, because it is a plane-type light source, uniform irradiation of a target object is operationally simple in comparison with the conventional light sources.

Because this device requires only a small operating current, it can be operated with dry cell batteries (Fig. 2). When the device is driven by stepping up the voltage obtained from 4 AA-size batteries connected in series, stable operation is possible for several hours without using a large power supply device. Thus, the device is easy to handle and is expected to open the way to application in new fields in which the use of conventional light sources had been limited.

Increasingly high expectations are placed on low environmental load UV light-emitting devices which do not use mercury, as seen in the example of the RoHS Directive\* in the EU. We intend to take on the challenge of achieving higher performance in this prototype device in order to meet these social needs.

References:

- K. Watanabe et al., Nature Materials 3, 404 (2004).
- K. Watanabe et al., Nature Photonics 3, 591 (2004).

\*RoHS Directive: Regulations on harmful substances contained in electrical and electronic devices adopted in the EU in 2006; regulates 6 substances including mercury, etc



Fig.2 Far UV light source with drive by dry cell batteries; the enlarged view shows the prototype light-emitting device. The blue line shown by the arrow is the light output part. A weak visible light component (400nm), which is emitted together with the intense far UV, appears as bluish-white.

## Graphene-based Quantum Devices

### — Coupled Quantum Dot Device —

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Graphite, which is an extremely familiar material that is used in pencil leads and other everyday applications, is a layered material consisting of stacked atomic monolayers (one-atom thick sheets called “graphenes”) of carbon atoms arranged in a honeycomb lattice. Recent research has revealed that one or few-layer graphene sheets show high carrier mobility at room temperature. As a result, graphene sheets have attracted strong interest as a material for novel electronic devices. At present, active research is underway on mass production of graphene sheets and the creation of integrated nanodevices.

In this research, we fabricated a coupled quantum dot device comprising two lateral quantum dots by applying a nanofabrication process to graphenes. Quantum dots have a structure in which electrons are confined in a microscopic space and, as a result, have a discrete energy state. A system of two quantum dots which have been placed in close proximity and contain either electrostatic- or tunnel-coupled electrons is called a coupled quantum dot. Because the number of electrons in a quantum dot, the coupling state between the electrons, and other properties can be controlled artificially using external voltages, etc., high expectations are placed on the application of coupled quantum dots to fundamental devices for novel functional electronics.

The devices which were actually used in these experiments were all fabricated on a single graphene sheet

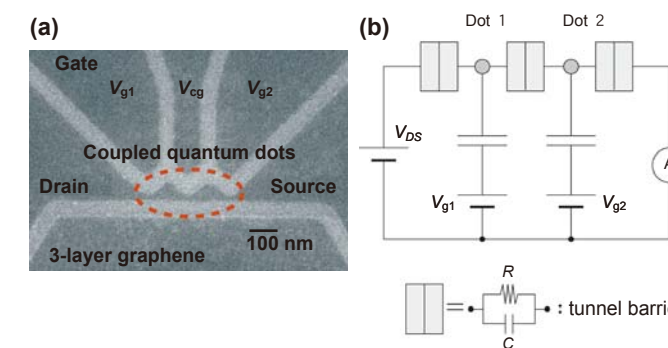
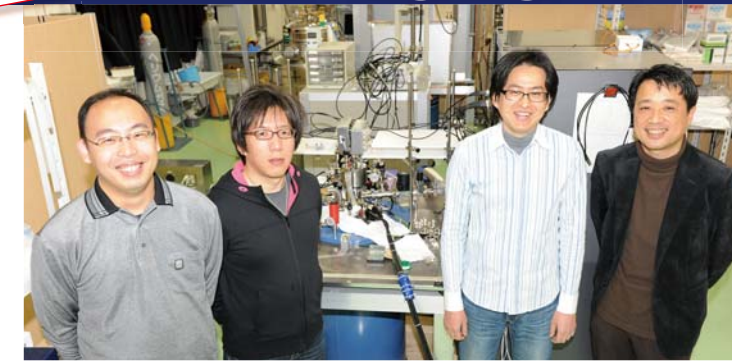


Fig.1 (a) Scanning electron microscope image of the structure of the graphene-based coupled quantum dot device. The parts shown in dark gray are the 3-layered graphene sheet; those in light gray are parts of the graphene sheet which were cut away by the nanofabrication process. (b) shows an equivalent circuit diagram of the device.



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(3-layered graphene sheet, thickness: approx. 1nm) using a nanofabrication technique. In Fig. 1(a), the triangular areas enclosed by the dotted line correspond to two quantum dots connected in series. In order to flow a current to the quantum dots, the two quantum dots are joined to the electrode areas (source, drain electrodes) of the graphene sheet by way of an extremely small region (hourglass-shaped part connecting the electrode and quantum dot). When various voltages were applied from two gate electrodes ( $V_{g1}$ ,  $V_{g2}$ ), we found that a current flowed only under certain determined voltages, as shown in Fig. 2. This means that the electron current can be adjusted and the number of electrons in the two quantum dots can be controlled in one electron units by independently changing the voltages  $V_{g1}$  and  $V_{g2}$ . Furthermore, this research also confirmed that the strength of coupling between the quantum dots can be controlled by the gate voltage, and thus succeeded in demonstrating operation as a coupled quantum dot device.

Because this research shows the potential for development of integrated nanodevices using a new carbon material, it is expected to contribute to progress in the development of nano quantum devices with novel functions.

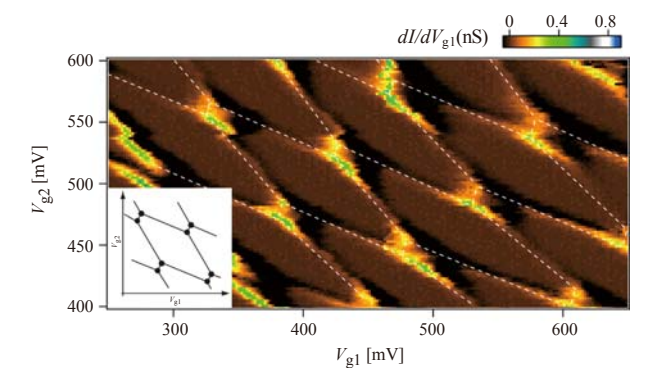


Fig.2 Diagram showing the flow of electrons as a function of the gate voltages  $V_{g1}$  and  $V_{g2}$ , which connected to the two quantum dots respectively. No current flows through the parts in brown; currents flow only through the parts shown in yellow to green. The device has a hexagonally-shaped regular period, as shown by the white dotted lines. The inset figure at the lower left is a schematic diagram of the device period. Analysis showed that these two quantum dots operate as a coupled quantum dot system.

## Dr. Ajayan Vinu Receives the ISCB Award for Excellence

(Jan. 15, 2010) Dr. Ajayan Vinu, Independent Scientist of MANA, had received Indian Society of Chemists and Biologists (ISCB) Award for Excellence, 2010 in the field of chemical science. ISCB is the biggest chemical society in India, and was founded in 1995 with the aim to promote and advance the cause of multidisciplinary research by providing a common platform for better cooperation and coordination.

ISCB award is one of the most prestigious awards in India which is normally given to the elderly professors who have done outstanding contribution in the field of chemical sciences.

Dr. Vinu is the first person to receive this award at the age of 33. The award ceremony was held on 15th of January in India and the award was given by Prof. David St. C. Black, the Secretary General of IUPAC (International Union of Pure and Applied Chemistry), University of New South Wales, Sydney, Australia.



Dr. Vinu and Prof. David St. C. Black (at right)

## Establishment of the Innovative Center of Nanomaterials Science for Environment and Energy

(Nov. 30, 2009) NIMS recently established the Innovative Center of Nanomaterials Science for Environment and Energy. The aim of the new unit is to conduct basic and generic research related to new materials for solving environmental and energy problems. It will be accomplished in cooperation with industry, academia, and governmental agencies, and by convergence of high accuracy theoretical analysis of surface/interfacial phenomena and advanced measurement techniques for dynamic observation of surface/interfacial nanostructures and reactions. The target fields are solar cells, photocatalysts, rechargeable batteries, and fuel cells.

The Center will be constructed by the "Program for Development of Environmental Technology Using Nanotechnology" of Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT), in order to promote basic and generic research of environmental technologies by bringing together leading researchers from home and abroad. NIMS has been selected as the host organization. The Center will conduct research to solve various problems in the above-mentioned four target fields, by achieving higher efficiency and securing safety, etc., to protect the environment and ensure stable supplies of energy.

## NIMS New Partnership

(Dec. 14, 2009) The NIMS Fuel Cell Materials Center concluded a memorandum of understanding (MOU) for "Key Materials of Fuel Cells" with Center of EMO (electrical, magnetic and optical) Materials and Nanotechnology College, National Taipei University of Technology in TAIWAN. It was agreed that the two institutions shall cooperate on "Key Materials of Fuel Cells" such as exchange of researchers, exchange of information, joint supervision of Master and PhD students, joint research proposals and implementation of cooperative research. In order to carry out the cooperation and utilize the results achieved, detailed plan shall be formed through consultation between the two partners. This memorandum is effective for five years.



From left: Prof. Yung-Fu HSU (NTUT, Group Leader), Prof. Sea-Fue WANG (NTUT, Managing Director), Dr. Chikashi NISHIMURA (NIMS, Managing Director) and Dr. Toshiyuki MORI (NIMS, Deputy Managing Director) at the signing ceremony.

### The 9th NIMS Forum The 8th International Symposium on Nanotechnology (JAPAN NANO 2010) at Tokyo Big Sight.

The 9th NIMS Forum will be held on Feb. 17th to introduce technologies that challenges the problems on environment and energy (only in Japanese).

Also, JAPAN NANO 2010 "Challenge of Nanotechnology for Energy and Environment" will be held on Feb. 19th (Japanese-English simultaneous interpretation).

For more details on JAPAN NANO 2010: <http://nanonet.mext.go.jp/japannano/2010/ENG>