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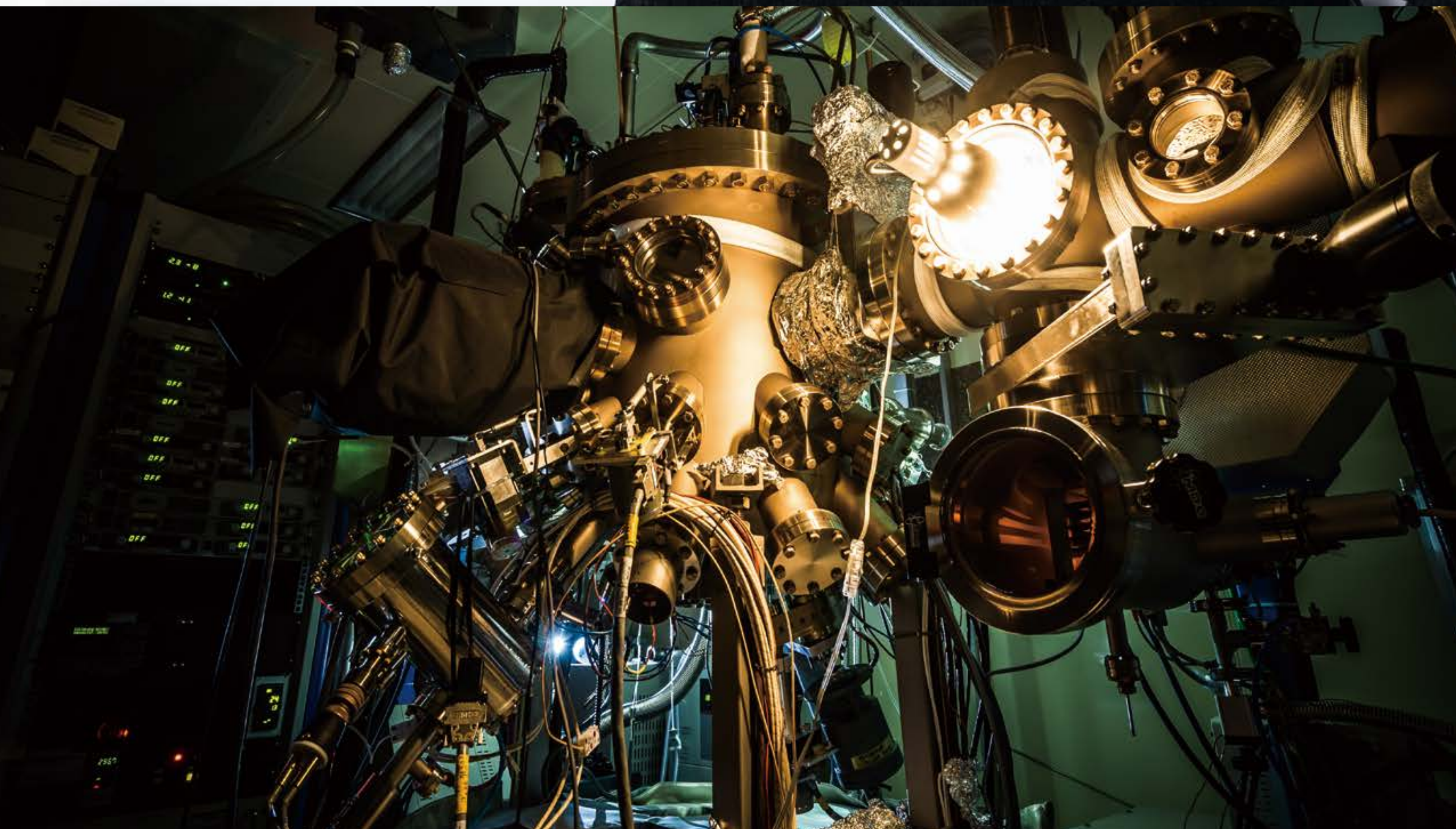
INTERNATIONAL

Research Center for Functional Materials: Part 1

Discovering "function X"

Novel materials and functions for a more affluent and comfortable society



Research Center for Functional Materials: Part 1

Discovering "function X"

Novel materials and functions for a more affluent and comfortable society

Our prehistoric ancestors painted lively pictures on cave walls.
Their creativity and the invention of paints enabled them to produce these artworks, which are still appealing to people today.

Prehistoric people discovered the color-generating "functions" of soil and crushed rocks which reflect light of various colors. Their great discovery led us to vividly colored, magnificent and long-lasting wall paintings.

Humans have skillfully exploited functions of various materials to enrich their lives and society and create new values.
Discoveries of novel functional materials periodically led to world-changing technological inventions, such as incandescent lightbulbs, light-emitting diodes and transistors.

Scientists at NIMS Research Center for Functional Materials—who are experienced with and knowledgeable in organic, inorganic and metal materials—are searching for potentially world-changing material functions to make society more comfortable and solve various global issues.

They are pursuing the development of next-generation devices exploiting the potential of various "functions X"—such as miniaturized, energy-efficient ultimate semiconductor devices and cryptographic devices capable of completely preventing eavesdropping—by investigating the fundamental properties of functions, taking creative approaches and using advanced techniques to control electrons and molecules.

Special Interview

World-changing materials and materials for the future

At the Research Center for Functional Materials (RCFM), specialists in organic, inorganic and metal materials engage in various R&D activities. RCFM researchers leverage the knowledge and know-how of their predecessors to produce innovative materials. We asked RCFM Director Naoki Ohashi about the latest trends in the development of functional materials and the strength of the RCFM.

Developing high-performance, lightweight, slim, compact and energy-efficient devices using functional materials

—First, how do you define functional materials?

As the name implies, functional materials have certain characteristics vital to everyday life. By this broad definition, any material could be called a functional material. However, our definition is more specific: functional materials are materials that exhibit physical or chemical responses to external stimuli, such as light, electron and heat. On the other hand, there is another category called "structural materials." They are different from functional materials in that they are required to remain unchanged and stable in response to external stimuli.

Let me illustrate the definition of a functional material using a real-world example. Paint—which has a history dating back to early human cave paintings—can be considered a functional material. The particles that constitute paint are optically functional materials because of their "function" of generating colors by reflecting and absorbing external light.

Many other materials, such as glass and plastics, can also be viewed as functional materials. I believe that the term "functional material" probably dates back to the time when semiconductor devices, such as transistors, first appeared. Since then, research and development related to functional materials have made great progress, enabling the performance of computers and other digital devices to be enhanced while reducing their weights and sizes. The advent of smartphones is a good example of this.

Some of the functional materials that have revolutionized society in recent years include the conductive polymers and semiconductors used in blue LEDs. It is well known that both materials were invented by Japanese scientists, earning them Nobel Prizes.

—I assume that the society needs have changed over time. What kinds of functional materials are currently being developed?

In the past, the invention of new materials was driven by new scientific discoveries. However, as science and technology advanced and society became richer, the development of new materials has increasingly been inspired by social issues and needs in recent years.

A particularly urgent social issue these days is the need to reduce CO_2 emissions by increasing the energy and thermal efficiency of various systems. An important key concept in the development of functional materials today is "enabling devices to perform their functions using as little energy as possible." It is important in this regard to reduce the amount of heat generated by computers and effectively reuse conventionally wasted energy, for example. Efforts also have been made to increase the performance of various devices to achieve faster processing, safer communication and so on.

The RCFM is the largest research center in NIMS at which scientists address the types of issues mentioned above. An array of spe-

Naoki Ohashi

Director of the Research Center for Functional Materials (RCFM)

Leader of the Electroceramics Group, RCFM
Leader of the Wide Bandgap Materials Group, RCFM
Leader of the Semiconductor Nano-interfaces Group, RCFM

cialists in organic, inorganic and metal materials conduct research on a wide variety of materials, such as semiconductors, ceramics and biomaterials (see the RCFM organizational chart on p. 7). SiAlON phosphors are an outstanding example. White LEDs, now widely used as a liquid crystal panel component, are composed of SiAlON phosphors and blue LEDs. We are continuing to conduct R&D on SiAlON phosphors to further increase their energy conversion efficiency and brightness. Other projects at the RCFM include the development of biocompatible, medical adhesive materials using cod gelatin and the development of foldable displays composed of organic-metallic hybrid polymers. We are striving to develop these materials to make society more affluent and comfortable.

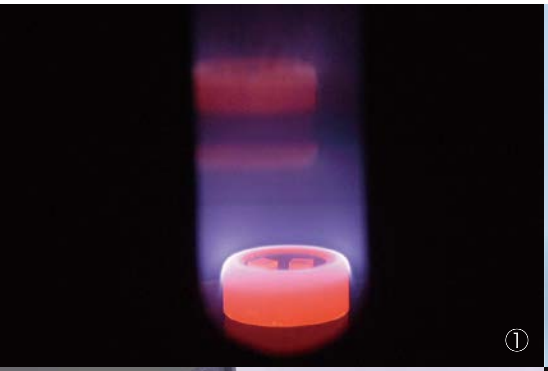
—What are the latest, most attention-grabbing research results?

Diamonds are attracting a great deal of attention for their potential to improve the energy efficiency and performance of various devices. Due to their high thermal conductivity and capacity to withstand high voltages, diamonds show promise as the "ultimate semiconductors." Tokuyuki Teraji of the RCFM has been researching and developing diamonds of exceptional purity and quality (see p. 8) which are drawing the attention of researchers all over the world. In addition, Takaaki Mano is developing quantum dot devices that may enable completely secure quantum cryptographic communication (see p. 10), and Masafumi Yoshio is applying liquid crystalline molecular materials—composed of organic-inorganic hybrid materials—to the development of luminescent materials, etc. (see p. 12). All of these materials have the potential to serve as next-generation materials.

In addition to these efforts, NIMS, as a specialized organization in materials research, also has the important mission of identifying the basic physical mechanisms of various materials. The development of new materials requires accurately understanding and estimating the crystalline structures and electron states within these materials. For example, Taichi Terashima is investigating the electron states of iron-based superconductors in a basic research project, which will be featured in this NIMS NOW issue. His findings may facilitate understanding of the currently unknown mechanisms involved in superconductivity (see p. 14).

When promising new materials are discovered, it is critical that effective and practical methods of producing them be developed. Many issues need to be resolved before new materials can be successfully integrated into devices. For example, materials need to be properly shaped and sized, and techniques must be found to produce them at reasonably low cost and consistent quality. Thus, the RCFM also works to develop practical processing techniques for materials (to be covered in the next NIMS NOW issue).

Supporting an aging society with a declining birthrate using high-performance sensors and soft electronics



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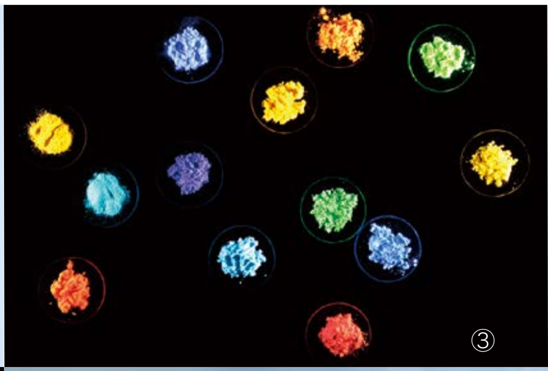

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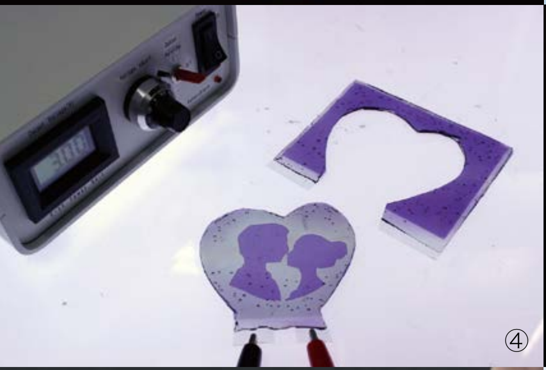

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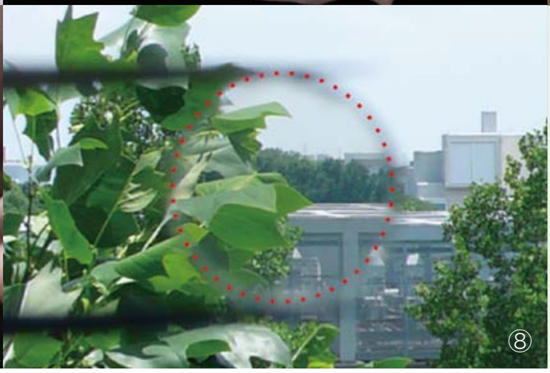


⑧

①Diamond synthesis using microwave plasma
②YAG single-crystal phosphor ingot. This phosphor is ideal for use in ultra-bright, high-power white lighting, and has superior temperature characteristics.
③SiAlON phosphors, including a red phosphor which enabled the development of white LEDs
④Polymer-based display with electrochromic properties, which can be cut into desirable shapes
⑤Polycapture, a high-performance oil adsorbent which enables extraction of flammable gases from water produced in oil fields
⑥Flexible, thin-film organic solar cells capable of efficient photoelectric conversion
⑦Cod gelatin, a promising medical adhesive material, remains in liquid form at room temperature, offering ease of use.
⑧Transparent hydroxyapatite ceramics produced at 850°C using a spark plasma sintering technique

—What are the prospects for functional material R&D in the future?

I have high expectations for the development of high-performance sensors vital to autonomous driving and robotics technologies. I am also focusing my attention on soft electronic materials. If electronic materials with muscle-like elasticity can be developed, they could be used to create energy-efficient robots capable of moving flexibly and smoothly, like real living organisms.

Functional material R&D has thus far assumed that functional materials would be used in hard devices, such as computers. In future studies, high-performance sensors may be combined with soft electronics to develop systems and robots able to provide intimate support in the everyday life of an aging society with a declining birthrate.

—What are the characteristics and strengths of the RCFM in relation to these visions?

It takes a very long time to discover materials and structures which are precursors to novel functional materials. The RCFM offers an environment that allows full dedication to this type of study. For example, we have been continuously engaged in research on diamond devices for nearly 30 years and on quantum dots for nearly 20 years, enabling us to accumulate a great deal of knowledge, skills and know-how. This is how we consistently generate research results that astonish the world.

Another advantage of the RCFM is that we have a group of engineers capable of properly operating the state-of-the-art characterization and testing equipment, which our status as a national research institute has enabled us to acquire. These engineers and instruments are expected that they may increase opportunities for serendipity, such as the chance of discovering unexpected and useful material functions which have gone unnoticed.

The RCFM's greatest strength is that it is staffed with researchers with expertise regarding a wide range of materials, from organic to inorganic. A fundamental prerequisite for research is appropriate human resources. New ideas often emerge through interactions between researchers. The RCFM has developed an interdisciplinary environment allowing highly experienced specialists to engage in stimulating interactions. We hope to take advantage of the resources available at the RCFM to create new materials for a more affluent and comfortable society.

(by Kumi Yamada)

RCFM organizational chart

Research Center for Functional Materials

Electric and Electronic Materials Field

Power semiconductor devices
High-Sensitive sensors

- Electroceramics G.
- Ceramics Surface and Interface G.
- Wide Bandgap Materials G.
  - ★High-Purity diamonds, p. 8
- Semiconductor Nano-interfaces G.
  - ★Liquid crystalline molecular materials, p. 12
- High-Temperature Superconducting Wire G.
- Low-Temperature Superconducting Wire G.

Optical Materials Field

LEDs

- Optical Single Crystals G.
- Sialon G.
- Colloidal Crystal Materials G.
- Nanophotonics G.
- Epitaxial Nanostructures G.
  - ★Quantum dots, p. 10
- Plasmonics G.

Functional Powder and Advanced Ceramics Field

- Field-Assisted Sintering G.
- Fine Particles Engineering G.
- Ceramics Processing G.

Thin speakers

Organic Molecules and Polymers Field

- Molecular Design and Function G.
- Electronic Functional Macromolecules G.

Flexible devices

Biomaterials Field

- Polymeric Biomaterials G.
- Bioceramics G.
- Cellular Functional Nanobiomaterials G.
- Nanomedicine G.
- Tissue Regeneration Materials G.

Medical materials

Quantum Materials Field

- Quantum Transport Properties G.
  - ★Iron-based superconductors, p. 14
- Quantum Solid State Materials G.
- Superconducting Materials Synthesis G.
- Strongly Correlated Materials G.
- Superconductor Quantum Phase Engineering G.

Quantum computers

Exploring Function Field

- Magnetoelectric Crystal G.
- High Pressure G.
- Carbon Composite Materials G.
- Functional Clay Materials G.

Searching for new functions

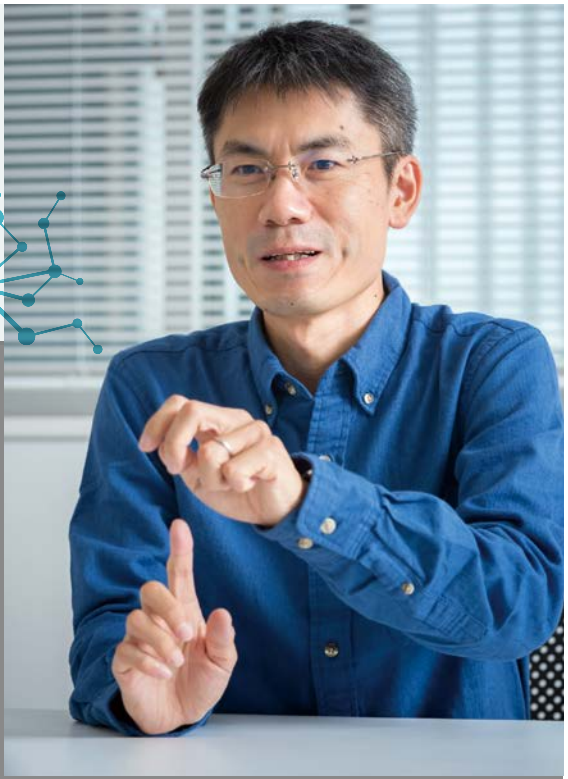
* G. = Group
* ★: research project featured in this issue

Discovering

Function X = withstands high-voltage + controlling electron spin with high accuracy

with high-purification technique

Developing innovative devices with highest quality diamond in the world



Diamonds—one of the most valued gemstones—have recently been drawing a great deal of attention as the "ultimate semiconductors" due to their capability to withstand high voltages and their excellent electron spin properties. Tokuyuki Teraji is involved in research and development of power semiconductor devices and quantum devices with the technique of developing single-crystal diamond thin films that are high in purity and quality.

Tokuyuki Teraji
Principal Researcher,
Wide Bandgap Materials Group,
Research Center for Functional Materials

Electronic application requires high purity and quality

Diamonds have fascinated humanity since ancient times. Their hardness led to popularity as an industrial abrasive when synthetic diamonds became available in the 1950s. Diamonds have also been the focus of attention in recent years as functional materials with high thermal conductivity and other outstanding properties. The application of diamonds in electronics has been studied particularly intensely.

In fact, diamonds act as supreme semiconductors. The band gap of diamonds is 5.5eV—five times greater than that of silicon, a conventionally used semiconductor material. Wide band gap semiconductors are capable of reducing the number of thermally excited charge carriers crossing the band gap and are therefore able to operate at high temperatures. In addition, the dielectric strength—an indicator measuring the insulation resistance of electronic circuits while voltage is applied—of diamonds is 30 times greater than that of silicon. The use of diamonds may therefore enable the development of thin, compact and energy-efficient power semiconductor devices. Thus, diamonds show promise as the "ultimate semiconductors" for use in power semiconductor devices. However, the high dielectric strength of diamonds needs to be verified experimentally before they can be used as semiconductors. These experiments require the creation of high-purity, high-quality single-crystal diamonds. Diamond crystals of similar quality will also be necessary for application to quantum devices. Tokuyuki Teraji is a world leader in the synthesis of single-crystal diamond thin films.

NIMS leads applied research on diamond semiconductors

The conventional method of synthesizing artificial diamonds has been the use of high pressure in a manner similar to the conditions under which diamonds form naturally. This method, however, is prone to contamination with impurities such as nitrogen from the air and boron in carbon source. Although such contamination is irrelevant for diamonds used in jewels and tools, it is unacceptable for diamonds to be used as semiconductor devices. Teraji avoids this problem by using a technique called microwave plasma chemical vapor deposition (MPCVD), whereby a diamond substrate in a vacuum chamber is exposed to methane gas—a source of the carbon atoms—triggering the growth of a crystal diamond thin film on the substrate (Figure 1). Decomposition of methane gas—which is composed mainly of hydrogen—using plasma is the crucial process enabling diamond thin film growth. This method was originally developed by the National Institute for Research in Inorganic Materials (the precursor to NIMS), and they succeeded in growing a diamond thin film under low pressure for the first time in the world in the 1980s using it.

Teraji said, "The use of a vacuum chamber in the MPCVD technique enables the synthesis of very pure diamond thin films.

However, single-crystal diamonds to be used in power semiconductor devices require even higher purity, with a maximum impurity concentration of approximately 0.1 ppm (1 part per 10 million). To meet this high standard, my colleagues and I designed a diamond growth system capable of creating ultrahigh vacuum conditions—a feature unavailable in commercial products. We then repeatedly enhanced the purification capabilities of the system by strengthening its vacuum evacuation unit. As a result, we were able to meet the high-purity standard necessary for the first time in the world."

Following this success, Teraji has received requests from researchers all over the world to synthesize diamond samples for use in power semiconductor device prototypes. Teraji is also pursuing the synthesis of diamonds capable of withstanding voltages higher than those silicon carbide—already in practical use as a power semiconductor material—can withstand. To achieve this, Teraji is using a creative impurity doping approach to synthesize high-purity diamond thin films with other desirable properties, such as high crystalline quality and controlled electrical conductivity.

While Teraji was making steady progress in creating high-purity, high-quality diamonds, he received requests to synthesize diamonds of even higher purity for use in quantum devices.

Achieving the world's highest purity

Quantum devices perform computations by making use of the properties of electron spin. Controlling spin states can normally be achieved only at temperatures approaching absolute zero. However, it was discovered in Germany in 1997 that spin states in diamonds alone can be controlled at ordinary temperatures. This discovery rapidly increased scientists' interest in applying diamonds to quantum devices. This spin is known as nitrogen-vacancy (NV) center. As part of this movement, Teraji undertook the challenge of synthesizing diamond thin films for use in quantum devices at the request of many overseas researchers. The level of purity required was extremely high. Teraji explained, "I had to increase the purity of diamonds by a factor of 10 or greater compared to the purity achieved for use in power semiconductor devices. This meant that the maximum impurity concentration had to be approximately 1 ppb (one part per billion). In addition, I had to perform isotopic enrichment to maximize the ^{12}C to ^{13}C ratio in diamonds because the nuclear spins of ^{13}C atoms produce noise which makes controlling electron spin difficult."

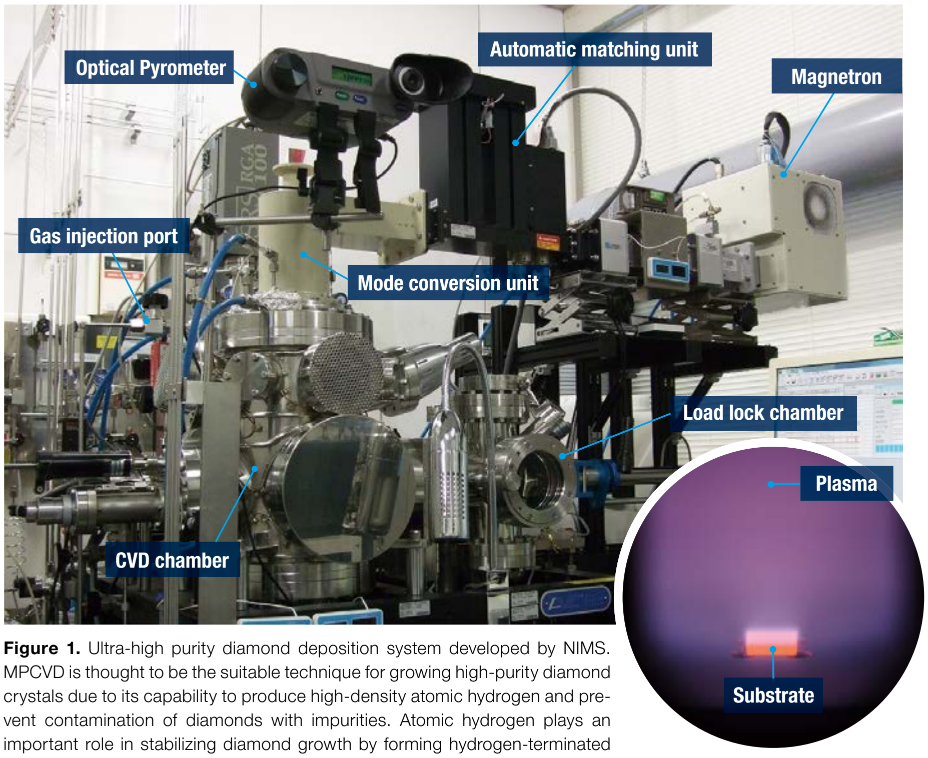


Figure 1. Ultra-high purity diamond deposition system developed by NIMS. MPCVD is thought to be the suitable technique for growing high-purity diamond crystals due to its capability to produce high-density atomic hydrogen and prevent contamination of diamonds with impurities. Atomic hydrogen plays an important role in stabilizing diamond growth by forming hydrogen-terminated diamond surfaces.

Teraji made various enhancements to the MPCVD system. For example, he introduced a load-lock chamber that is connected to growth chamber and sample materials are pre-evacuated in this chamber. It enabled sample transfer in the growth chamber without exposing them to ambient air, thereby minimizing their contamination with external impurities. He also strived to acquire isotopically enriched carbon gases and installed a gas purification unit. As a result, he was able to reduce the concentration of nitrogen—a main impurity for diamond—to approximately 0.1 ppb (one part per 10 billion), which was only one-tenth of the target value, and achieved ^{12}C concentration of 99.998%. Finally, the single-crystal diamond crystals he synthesized recorded the world's highest values for both purity and isotopic enrichment for the bulk material (Figure 2). "The diamond samples we have created have been used in various research projects, such as the development of high-sensitivity, high-spatial-resolution quantum magnetic sensors capable of operating at room temperature and ordinary pressure. We will continue to enhance our techniques for synthesizing single-crystal diamond thin films applicable to both power semiconductor devices and quantum devices," said Teraji enthusiastically.
(by Kumi Yamada)

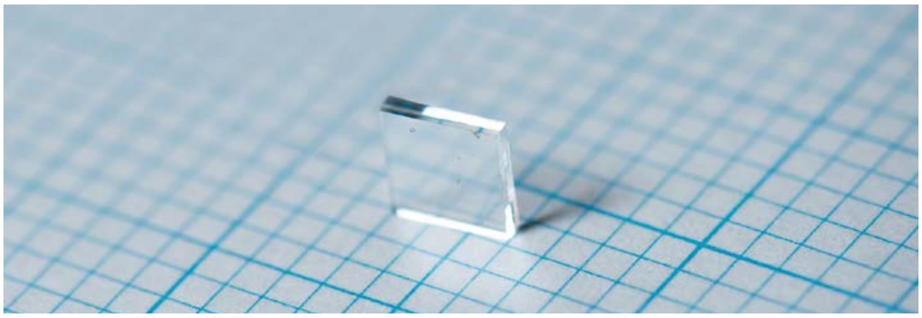


Figure 2. A super-high-purity diamond crystals created by Teraji. Its purity is among the highest in the world, with a nitrogen impurity concentration of 0.1 ppb or less and a ^{12}C concentration of 99.998%.

T. Teraji, J. Appl. Phys. 118, 115304 1-8 (2015). DOI: 10.1063/1.4929962

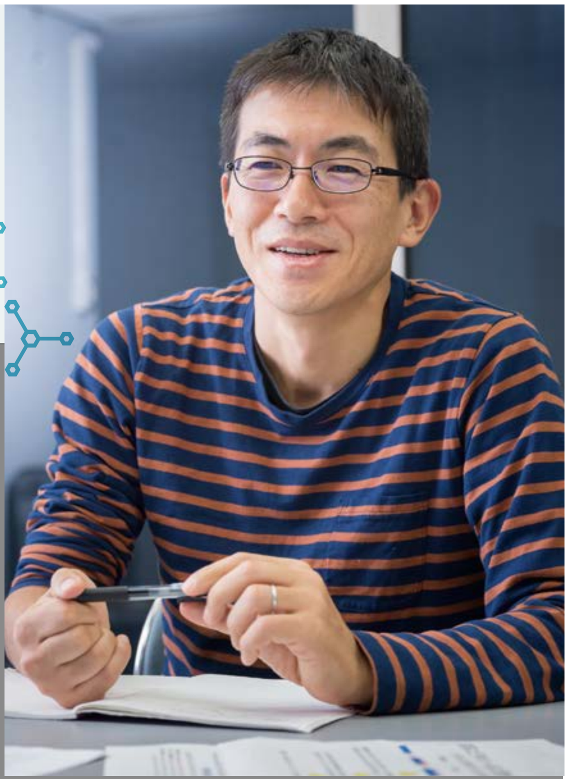
Discovering

Function X = entangled photon pairs emission

for realizing quantum cryptography

Quantum dots for safe and secure communication

A quantum dot is a tiny semiconductor, approximately 10 nanometers in size. Quantum dots are already in practical use in semiconductor lasers, and research and development is underway to pursue their potential applications in various fields, such as solar cells, photodetectors and high-definition displays. Takaaki Mano is developing quantum cryptography, a promising next-generation communications technology. Mano fabricates quantum dots using a droplet epitaxy technique—which utilizes advanced technologies of crystalline thin film growth—developed by NIMS.



Takaaki Mano
Principal Researcher,
Epitaxial Nanostructures Group,
Research Center for Functional Materials

Growing expectations for quantum dots

Quantum dots are tiny semiconductor particles (approximately 10 nanometers in size) capable of trapping electrons. Electrons exhibit various unusual phenomena when tightly confined. For example, electrons emit and absorb light of different wavelengths depending on the size of the quantum dot in which they are confined. Many studies are attempting to apply these properties to develop backlighting devices for liquid crystal displays and solar cells.

Research and development of novel optical and electronic devices using quantum dots is being undertaken all over the world. Takaaki Mano is pursuing the application of quantum dots to quantum cryptography, an ultimately secure communications technology that may completely prevent eavesdropping.

Currently, quantum cryptography is only applicable to short-distance communication. Its application to long-distance communication requires utilization of so-called "entangled photon pairs" with mysterious properties. To enable quantum dots to emit entangled photon pairs, new crystal growth techniques need to be developed to precisely control the shape of the quantum dots.

Long-distance quantum cryptography using quantum dots

Quantum cryptography is a promising, next-generation optical communication technology. It exploits unique "quantum entanglement" phenomena exhibited by pairs of specific quantum particles. The interaction of a pair of entangled particles is such that the quantum state of one particle cannot be described independently of the other, even when the particles are separated by a large distance. Technology based on this observation could potentially enable eavesdropping to be detected quickly, fully protecting confidential information and preventing information leakage.
In quantum cryptographic communication, each photon—a type of elementary particle—carries information through optical fibers. The transmission distance of photons is currently limited to several tens of kilometers due to their fragile quantum states. To extend the distance, proper placement of relays called quantum repeaters compatible with entangled photon pairs is required. Mano is attempting to develop quantum repeaters using quantum dots.

Mano said, "When a quantum dot confines one electron-hole pair, it emits a single photon. Similarly, when a quantum dot confines two electron-hole pairs, it emits two photons almost instantaneously. The quantum states of these two photons—if emitted from an adequately symmetrical quantum dot—interact and become entangled. But the lack of the growth technique to create isotropic quantum dots, that are perfectly spherical or equilaterally triangular, was the problem."

Several techniques can be used to fabricate quantum dots, including the Stranski-Krastanov (SK) method used to grow crystalline thin film semiconductors epitaxially. The SK method enables self-assembly

Figure 1. GaAs quantum dot fabrication process using droplet epitaxy technique

Atomic force microscopy images (top) and schematic diagrams (bottom)

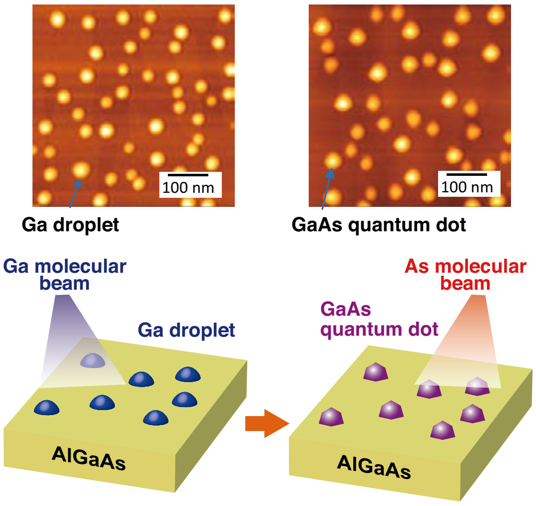
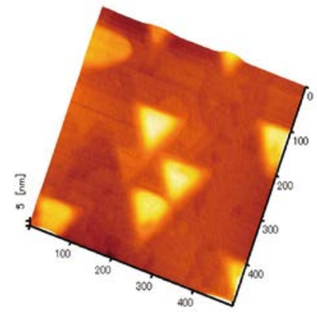
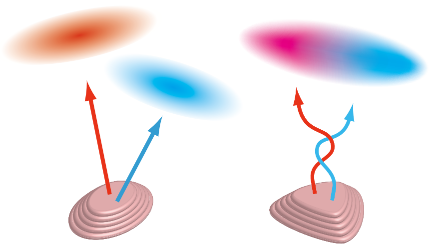


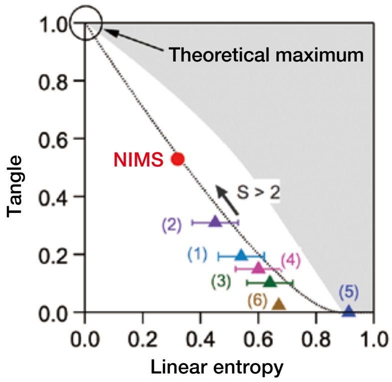
Figure 2. GaAs quantum dots on the (111) A surface and an entangled photon pair



Atomic force microscopy image. The three-fold rotational symmetry of the GaAs (111)A surface enables the formation of isotropic quantum dots.



Schematic of an entangled photon pair. The successful fabrication of the isotropic quantum dots led to the development of an entangled photon source which demonstrated the world's highest performance.



Performance comparison between the entangled photon sources developed by Mano's group and those of others. (1) through (6) represent photon sources of other groups. The photon source of Mano's group was greatly superior in performance to the others. The vertical and horizontal axes represent quantum strength and degree of quantum state entanglement, respectively.

of quantum dots on a semiconductor substrate, leveraging the lattice distortion which occurs when crystalline materials with different lattice parameters are grown together. However, it is difficult to form isotropic quantum dots using this method.

An alternative, superior quantum dot fabrication method has been developed. "Nobuyuki Koguchi of the National Research Institute for Metals (the precursor to NIMS) developed a novel droplet epitaxy technique in 1990 and we made various modifications to it over time in NIMS," Mano said. "In this technique, a gallium arsenide (GaAs) or indium phosphide (InP) substrate is irradiated with a beam of gallium (Ga) or indium (In) to form nanoscale, hemispherical liquid metal droplets on the substrate. Arsenic (As) is then supplied to the droplets. This supplied As bonds to the Ga or In in the droplets to form GaAs or InAs crystals, which constitute quantum dots (Figure 1). Unlike the SK method, this technique allows the use of lattice-matched substrates. Moreover, the technique enables to form isotropic quantum dots."

Taking advantage of the droplet epitaxy technique

After much trial and error in efforts to extend the distance of quantum cryptography, Mano succeeded in 2013 in developing an entangled photon source using highly symmetrical quantum dots formed on a GaAs(111)A substrate, which demonstrated the world's highest performance (Figure 2).

The entangled photon source Mano developed, however, emits wavelengths of approximately 700 nanometers—incompatible with silica optical fibers currently in use, which operate at a wavelength of 1.55 micrometers (near-infrared range) to minimize optical power loss. Thus, an entangled photon source will need to be modified to enable emission in the near-infrared range for it to be applicable within the current communications infrastructure. To achieve this, Mano initiated a new research project around 2015 to form InAs quantum dots on an InP(111)A substrate using the droplet epitaxy technique. "I needed to fabricate InAs quantum dots to generate near-infrared wavelengths," Mano said. "I initially formed quantum dots on GaAs substrates, but they did not emit the intense light at appropriate wavelengths. I then tried InP substrates whose lattice constant are closer to those of InAs, and was able to produce much better results. However, the cost of an InP substrate is two to three times that of a GaAs substrate, requiring creative approaches to reduce substrate costs and make the technology reasonably affordable."

Creating entangled photon emitting diodes

Mano is also undertaking another research project: an attempt to create quantum dot devices capable of emitting entangled photons when subjected to an electric current. The quantum dots he demonstrated in the 2013 experiment emitted entangled photon pairs when irradiated with light. To develop smaller, practical quantum dot devices, quantum dots capable of emitting entangled photons in response to electrical current injection, rather than light irradiation, are necessary. The development of electrically induced quantum dots—while still at a very basic research stage—may enable long-distance quantum cryptography in the near future. "I would like to explore various potential applications for the droplet epitaxy method, in addition to long-distance quantum cryptography," Mano said.

(by Kumi Yamada)

T. Kuroda, T. Mano, et al., Phys. Rev. B. 88 [4] (2013) 041306(R)-1 DOI: 10.1103/PhysRevB.88.041306

Discovering

Function X = selectively permeable and capable of multicolored luminescence which expands the field of application

Exploring the potential of flexible, energy-efficient liquid crystalline materials

Masafumi Yoshio
Principal Researcher
Semiconductor Nano-interfaces Group
Research Center for Functional Materials

Liquid crystalline materials—composed of self-assembled molecules—are capable of performing various functions. Masafumi Yoshio is attempting to apply liquid crystalline materials to a variety of new technologies, such as separation membranes, fuel cells and luminescent materials, by leveraging their unique properties.

Fluid and reversible liquid crystalline materials composed of self-assembled molecules

A liquid crystal—which is well known for its use in liquid crystal displays—is composed of orderly arranged molecules in a manner similar to solid crystals but is capable of flowing like a liquid (Figure 1). Masafumi Yoshio is researching and developing novel functional materials by leveraging certain properties of liquid crystalline molecules.

"The most striking characteristic of liquid crystalline materials is that they are composed of self-assembled molecules," Yoshio said. "Their orderly structures can be spontaneously formed through self-assembling processes involving molecules, atoms and ions; no artificial manipulation is necessary. This spontaneous process enables production of functional materials at low cost without relying on complex production processes. For example, I am currently studying gyroid structures—a very complex three-dimensional structures in which tiny holes run through it in many different directions. Although these structures are difficult to create by artificial manipulation, the use of self-assembly of liquid crystals with the proper molecular design as a key can allow us to fabricate the gyroid-structured materials much more simply (Figure 2)."

In addition, liquid crystalline molecules are loosely bound together by weaker forces of attraction—such as hydrogen bonds and van der Waals force—than covalent and metallic bonds. Therefore, the organized structures of liquid crystalline materials can easily be changed and recovered repeatedly. These fluid and reversible properties are also advantageous.

"I think these unique properties can be exploited to develop groundbreaking functions which are impossible to develop using existing materials," said Yoshio.

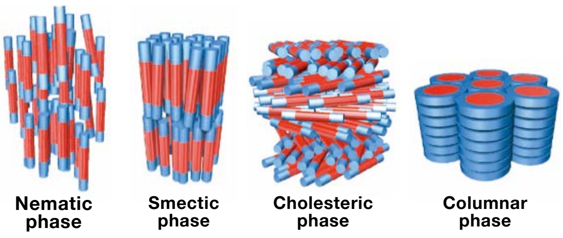


Figure 1. Liquid crystal phases
Liquid crystal displays employ elongated liquid crystalline molecules in the nematic phase. Other liquid crystal phases include the smectic phase in which elongated molecules form a layered structure, the cholesteric phase in which molecules form a helical structure, the columnar phase in which molecules assemble into cylindrical structures and the gyroid cubic phase in which molecules form a three-dimensional branched structure (Figure 2).

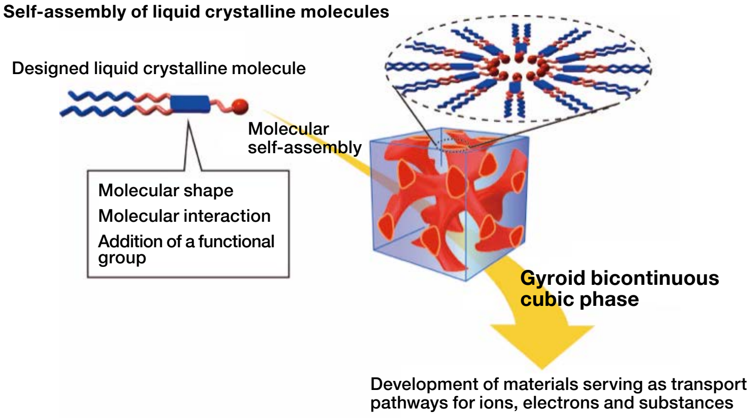
Enhancing selective permeability of separation membrane and fuel cell membrane

Yoshio is currently studying liquid crystalline materials that allow ions, electrons and specific substances to pass through them.

He is pursuing the application of gyroid-structured liquid crystalline materials to the development of separation membranes capable of converting seawater into fresh water by removing its salt content and other substances. A three-dimensional, isotropic gyroid structure is composed of an infinitely connected periodic surface—which is formed by wedge-shaped ammonium salt molecules—extending in many different directions. The separation membrane can effectively desalinate water as its hole sizes are such that small water molecules can pass through them while larger hydrated metal ions cannot. Unlike liquid crystalline materials with anisotropic columnar structures, those with isotropic gyroid structures allow target substances to continuously pass through them without the need to manipulate their molecular orientation at the macroscale, enabling them to be mechanically strong. In addition, fluid and reversible properties of liquid crystalline materials may be exploited to make the hole sizes of separation membranes adjustable. This approach has the potential to lead to the development of a versatile separation membrane compatible with substances of various sizes.

Gyroid-structured materials also may be applicable to fuel cells. Polymer electrolyte fuel cells (PEFC) currently used in automobiles are equipped with an ion exchange membrane between the cathode and anode. The PEFC generates electricity as hydrogen ions pass through the membrane. The conventional ion exchange membranes composed of Nafion polymers allow hydrogen ions dissolved in water to pass through them. Power generation capacity of fuel cells equipped with a Nafion membrane decreases when water evaporates at high temperatures. "To address this problem, I am developing a liquid crystalline material capable of allowing hydrogen ions to directly pass through it without requiring water. I think that replacing a Nafion membrane with this material will enable fuel cells to durably maintain their power generation capacities even at high temperatures," Yoshio said. This new material is currently being developed in the project titled "Development of anhydrous proton-conducting liquid-crystalline polymer membranes and their application in fuel cells," which will continue through March 2020. Yoshio is aiming to put the new material into practical use within several years.

Figure 2. Self-assembly of liquid crystalline molecules



Developing energy-efficient luminescent materials capable of changing colors by rubbing

Yoshio is also developing luminescent materials using liquid crystalline molecules.

Mechanochromic luminescent materials are capable of changing their colors when their crystalline structures are altered in response to mechanical stimuli, such as rubbing and shearing. The use of these materials—usually composed of crystalline organometallic complexes—however, is limited due to some disadvantages associated with crystalline materials, such as incapability to recover their crystalline structures once they are altered. By contrast, fluid and reversible liquid crystalline materials are capable of dramatically changing their luminescent colors by applying a low-level stimulus and easily recovering their original colors (Figure 3). In other words, Yoshio is attempting to create paint materials capable of changing their colors like chameleons do. Unlike solid crystals, fluid liquid crystals can easily be used to coat various objects. "I believe these desirable characteristics of liquid crystalline materials can be exploited to develop anti-counterfeit coatings that can be applied to soft materials, such as paper, and ship-bottom coatings capable of indicating friction damage levels by color change. The latter technology may facilitate the development of low drag hulls and early detection of damaged hull parts," said Yoshio.

At present, one type of liquid crystalline molecule can produce about two luminescent colors. Yoshio wants to increase that number. Luminescent materials capable of emitting light without using electricity are drawing a great deal of attention recently from people conscious about energy-saving and reduction of CO_2 emission.

"When I was a child, my father encouraged me to solve energy issues when I grow up to ease Japan's energy resource shortage. I still remember his advice today. I hope that the liquid crystalline materials I developed will be applied to fuel cells, coating materials and luminescent materials in the near future to live up to my father's teaching," said Yoshio with a renewed determination.

(by Kumi Yamada)

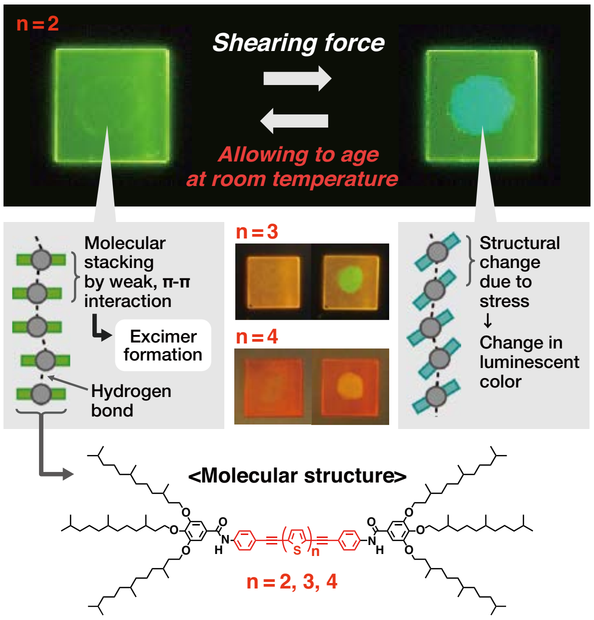


Figure 3. Mechanochromic luminescent liquid crystal

The liquid crystals—consisting of oligothiophene derivatives—are capable of changing their luminescent colors reversibly at room temperature in response to shearing and aging. When liquid crystalline molecules bind together by weak forces of attraction—such as π-π stacking interactions and hydrogen bonds—luminescent π-conjugated parts (the red part in the molecular structure) come into contact with one another, forming a light-emitting excimer.
Application of shearing forces prevents excimers from forming and causes π-conjugated monomers to emit light of different colors.

T. Kato, M. Yoshio, et al., Nat. Rev. Mats. 2 (2017) 17001-1 doi:10.1038/natrevmats.2017.1

Physical mechanism investigation

Vol.❶

Efforts to understand the origin of superconductivity

Measurement of electronic states of iron selenide (FeSe) superconductors

In the search for novel materials, it is vital to understand their fundamental physical mechanisms. In the Research Center for Functional Materials issues 1 and 2, we will feature two basic research developments with the potential to lead to the discovery of innovative materials. In this issue 1, we highlight efforts to understand the mechanisms of iron-based superconductors, which show promise as energy-efficient materials.

Taichi Terashima

Chief Researcher,
Quantum Transport Properties Group,
Research Center for Functional Materials

Although superconductors are promising energy-efficient materials due to their capability to conduct electricity without energy loss, it is enormously costly to cool materials to extremely low temperatures, preventing their widespread application. Taichi Terashima is working to understand the mechanisms of superconductivity to facilitate the discovery of materials that exhibit it at higher temperatures.

Terashima has been studying iron-based superconductors, which drew global attention when transition temperatures as high as 56 K (-217°C) were demonstrated a year after their discovery by Prof. Hosono of Tokyo Institute of Technology.

Among about 10 types of iron-based superconductors available, Terashima is particularly interested in iron selenide (FeSe) superconductors. Most iron-based superconductors undergo crystalline structural distortion and become antiferromagnetic when cooled to extremely low temperatures. These materials are assumed to become superconductive when subjected to pressure or doped with other elements, which suppresses the crystalline distortion and the antiferromagnetic state. However, unlike these iron-based superconductors, FeSe remains paramagnetic at extremely low temperatures and becomes superconductive even when no pressure is applied.

"I am trying to understand why only FeSe, and not other iron-based superconductors, becomes superconductive without pressure nor doping," Terashima said. He believes that the Fermi surface structure of FeSe may provide vital information to answer this question.

"Fermi surface structures—which indicate the highest energy level electron states—provide crucial information, such as electron flow patterns and the conditions required to generate superconductivity. Fermi surface structures can be estimated using first-principle calculations and in most cases, estimates are consistent with actual experimental results. However, inconsistencies between estimates and results were noted in some studies on iron-based superconductors. Therefore, I thought it was important to actually measure the Fermi surface structure of FeSe. I conducted experiments to determine the structure by measuring quantum oscillations," said Terashima.

Quantum oscillation measurements are performed under conditions in which a sample material is cooled to as low as minus 270°C and exposed to very strong magnetic fields. These conditions induce a quantum oscillation, in which electrical resistance and other properties of the subject material fluctuate between high and low values. The shape, size and the number of Fermi surfaces can then be determined by analyzing oscillation patterns.

Terashima succeeded in measuring quantum oscillations in FeSe for the first time in the world in joint research conducted in 2014 by the NIMS, Kyoto University, the Karlsruhe Institute of Technology in Germany and the National High Magnetic Field Laboratory in the United States. The measured number and sizes of the Fermi surfaces were found to be very different from the estimates (Figure). "I could not have successfully performed the measurements without the confidence my colleagues showed in my years of experience in this field by making high-quality sample materials and a facility capable of generating powerful magnetic fields available to me. I am currently discussing the cause of the discrepancy between the computational estimate and the actual measurements with theorists. We suspect that electron interactions are responsible which were not taken into account in the theoretical modeling. Because this finding may be the key to understanding the mechanism of superconductivity, we would like to continue pursuing our joint investigation," said Terashima.

(by Kumi Yamada)

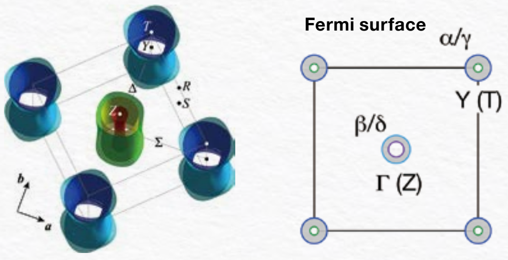


Figure. Discrepancy in the Femi surface structure between the computational estimates and actual measurements

The computations estimated the existence of two Fermi surfaces at each of the four corners of the square—called the Brillouin zone—and three Fermi surfaces at the center. By contrast, actual measurements found only one much-smaller-than-estimated Fermi surface at each corner and the center.

Note that the sizes of the Fermi surfaces in the actual measurement diagram are illustrated accurately while their shapes are not.

T. Terashima, et al., Phys. Rev. B. 90 [14] (2014) 144517-1 DOI: 10.1103/physrevb.90.144517

What would room-temperature superconducting materials mean to the world?

Text by Akio Etori

Illustration by Joe Okada (vision track)

Unlike a couple of decades ago, people looking for home entertainment can today easily download a feature film via the Internet in a few minutes. Dramatic advances in data storage and transfer technologies have made our lives more convenient. High-performance computers are vital to these technological advances. The development of silicon transistors—solid-state semiconductor devices—greatly enhanced computer performance.

Transistors replaced vacuum tubes as switches in computer circuits soon after being invented in 1948 by three researchers at Bell Laboratories in the United States.

Vacuum tubes at that time were very large, consumed large amounts of power and burnt out frequently. In contrast, early transistors were revolutionary by being much smaller and nearly failure-proof, leading to their eager adoption. The subsequent invention of integrated circuits (ICs) and large-scale integration (LSI) drove intensive miniaturization and integration of transistors, enabling computers to process large amounts of information.

In addition, the evolution of glass and plastic materials enabled the development of optical fibers which allowed the transmission of optical rather than electrical information.

Many types of materials, including those mentioned above, enabled high-speed, large-volume information transmission, making our lives more convenient.

What would be the next world-changing material? What I would like to see is a room-temperature superconducting material.

As is well known, superconductors have a remarkable property—their electrical resistance becomes zero under certain conditions. This property (or function) can be exploited to achieve great things.

MRI (magnetic resonance imaging) machines already in practical use are capable of forming clear brain images, and plans are underway to build high-speed magnetic levitation trains between Shinagawa and Nagoya in Japan.

Superconducting materials also have a major disadvantage, however. Superconductivity occurs only when these materials are cooled to extremely low temperatures. The first superconductor, discovered in 1911, demonstrated superconductivity at minus 269°C. A material exhibiting superconductivity at minus 243°C was subsequently discovered in 1986. Other materials with higher critical temperatures (about minus 100°C) have been discovered since then, but these temperatures are still unthinkably cold to ordinary people.

Thus, the use of superconducting materials requires the installation and operation of powerful cooling systems which are both tremendously labor-intensive and expensive.

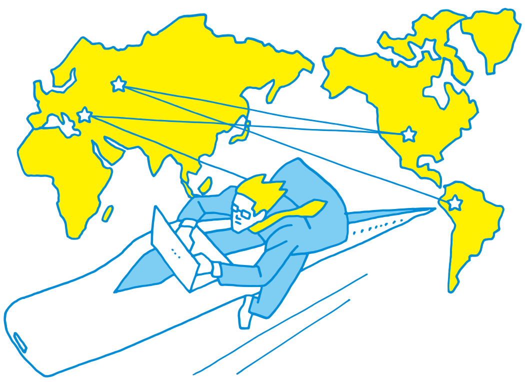
The discovery of materials capable of exhibiting superconductivity at room temperature would be a greater achievement than the invention of transistors. I wonder if such dream materials really exist on Earth.

A majority seem to be pessimistic about this possibility. However, many researchers are still investigating the mysterious superconducting mechanism. I am sure that the knowledge that will be obtained from these investigations will be useful in discovering and creating novel materials.

It would be very exciting to imagine the world after the discovery and invention of room-temperature superconducting materials and process them into long cables and large magnets.

I think room-temperature superconducting technology could revolutionize the world by enabling storage and long-distance transmission of electricity without energy loss and intercontinental operation of magnetic levitation trains.

Perhaps I am just fantasizing about unrealizable dream. However, dreams sometimes inspire people. As researchers study room-temperature superconductors, they might make some unexpected, but scientifically significant discoveries along the way. I believe that the power of dreams can move our society in a technologically desirable direction.



Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

NIMS NEWS

1 STAM MI-Forum website open

In November 2017, NIMS opened a STAM MI-Forum website.

STAM MI-Forum is a bidirectional site for scientists working on materials informatics (MI) provided by scientific journal Science and Technology of Advanced Materials (STAM). STAM MI-Forum website will provide a wide range of MI related papers published as Communications articles in STAM, ranging from essential information for beginners to the latest updates for professionals. As well as following ups by authors, readers can also use this site to provide information and points of discussion.

2 Eight NIMS Researchers as "Highly Cited Researchers 2017"

Eight NIMS Researchers, Dr. Yoshio Bando (Executive Advisor, MANA), Dr. Katsuhiko Ariga (MANA Principal Investigator [PI]), Dr. Dmitri Golberg (MANA PI), Dr. Takashi Taniguchi (Group Leader, Research Center for Functional Materials), Dr. Kenji Watanabe (Chief Researcher, Research Center for Functional Materials), Dr. Yoshihiko Takano (MANA PI), Dr. Yusuke Yamauchi (MANA PI) and Dr. Zhong Lin Wang (MANA PI), are announced to be Highly Cited Researchers 2017.

"Highly Cited Researchers" are the researchers ranking in the top 1% by citations for field and publication year in Web of Science, based on Clarivate Analytics's (Predecessor, Thomson Reuters) Essential Science Indicator database.

Hello From NIMS

Hello, my name is Thiyagu Subramani, and I am from Tamil Nadu, India. I am working as JSPS research fellow in the Nanostructured Semiconducting Materials group at MANA. I have been living in Tsukuba science city since November 2015. Before coming to Japan I was little bit worried because at that time my wife was 3 months pregnant. But after coming to Japan and joining NIMS, I was very much happy and also I felt like blessed with my wife's healthy pregnancy period. Later, when my son was born in University of Tsukuba Hospital, I really felt people in Japan are so nice and polite. I got lot of support from JISTEC (Japan International Science and Technology Exchange Center) and NIMS. NIMS have excellent facilities and world-class scientists, plus the freedom to pursue my own research ideas. My research focus on metal oxide based flexible silicon solar cells. Also there is an amazing program called ICYS (International Center for Young Scientists) in NIMS, by which young scientists are doing the research independently with their own research budget and the freedom. Fortunately, I could join ICYS researcher in this New Year of 2018. I am very thankful to Japan and NIMS to give me this opportunity and recommend the people around the world to visit Japan at least once in a lifetime.


Enjoying traditional party in Ninomiya house, Tsukuba


Enjoying snow and sakura in Ueno park


Thiyagu Subramani (Indian)
November 2015 to present
ICYS

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