International Center for Materials Nanoarchitectonics

Toward a better global future: Pioneering a new paradigm in materials development on the basis of "nanoarchitectonics"

MANA's purpose is to pioneer a new paradigm in nanotechnology by proposing and developing the novel concept of "nanoarchitectonics." Nanoarchitectonics is a system of material architectural technology that enables free creation of new material functions by controlling the arrangement and interactions of nano-sized units. Aiming at new materials that will support next-generation technologies in various fields, including energy and the environment, information and communications, and medicine, MANA has attracted global attention for its world-class research in the five fields of Nano-Materials, Nano-Systems, Nano-Power, Nano-Life and Nano-Theory.

Research Center's Information (FY 2015)

Center Director: Masakazu Aono
Principal Investigators (PI): 18 (including 8 overseas researchers and 2 female researchers)
Other Researchers: 179 (including 96 overseas researchers and 36 female researchers)
Research Support Staff: 10
Administrative Division:
  Administrative Director: Tomonobu Nakayama
  Administrative Staff: 18 (percentage of bilingual staff: 100%)
Satellites and Cooperative Organizations: University of California, Los Angeles, USA; Georgia Institute of Technology, USA; University of Tsukuba, Japan; French National Center for Scientific Research (Centre national de la recherche scientifique, CNRS), France; University of Montreal, Canada; University College London, UK; and others
URL: http://www.nims.go.jp/mana/

Nano Revolution for the Future

Major Research Achievements

1 Oxide nanosheets for next-generation electronic devices through nanoarchitetonics

MANA discovered high-k dielectric nanosheet with 1 ～ 2nm thickness using functional oxides such as Titanium oxide. A high-performance thin-film capacitor having the world's smallest size and the highest performance was successfully developed by stacking these nanosheets, nanosheet architectonics.

2 Atomic switch with synaptic operations of remembering and forgetting

The world's first "synaptic element" was successfully developed by using an "atomic switch" that forms a conducting path by transfer of metal atoms (ions) when a voltage is applied. This element autonomously reproduces the distinctive remembering/forgetting neural operations of the brain.

3 Development of electron microscope for *in-situ* measurement of nanomaterial functions

An "*in-situ* property measurement instrument" was developed by combining techniques for precise manipulation of individual nanomaterials with the outstanding high resolution performance of the transmission electron microscope (TEM). The relationship between nanostructure and physical properties of nanomaterials was successfully clarified by using this instrument.

4 Ultra-high sensitivity, ultra-compact nanomechanical sensor realizing "mobile olfaction"

An ultra-small sensor, "Membrane-type Surface stress Sensor (MSS)," which enables detection of various molecules with extremely high sensitivity was successfully developed. An industry-academia-governmental joint research framework, the "MSS Alliance," was launched to realize practical application and industrial standardization of olfactory IoT sensor systems.

5 Discovery of mechanisms for enhanced performance of thermoelectric materials

The importance of the interaction of charge carriers and magnons as a mechanism by which magnetism improves thermoelectric performance in $CuFeS_2$ magnetic semiconductor system materials was discovered. Performance enhancement was also realized by synthesis of nanosheets of thermoelectric materials.

Research Paper's Information

Number of Research Papers:	3316
Top 10% Papers:	37.1%
Top 1% Papers:	7.8%
Internationally Collaborative Research Papers:	46.2%

(Database: SCOPUS database, Elsevier B.V.)

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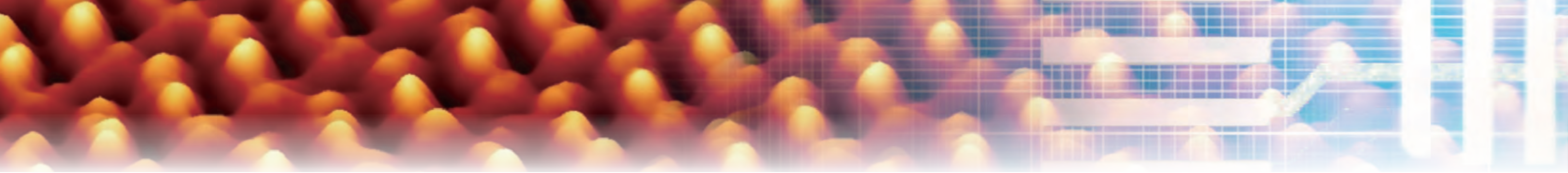
The world's thinnest superconductor: ordered metal atoms on a silicon surface



To continue sustainable development, the human race requires tireless pioneering of advanced technologies that achieve innovations in the food, resources and energy production, information processing and communication, medical diagnosis and treatment, and improvement and preservation of social infrastructure and the environment. However, many of these technologies will not be realized without proper new materials. In the last 30 years nanotechnology has achieved remarkable growth. But in recent years further evolution is required to enable nanoscale observation and manipulation of materials and making many important contributions to the development of new materials. Advancing beyond observation and manipulation, novel technologies are required that enable creation of materials with the desired functions by combining and assembling nano-scale materials.

However, because nanomaterials exhibit properties that are unimaginable in everyday world, realizing these technologies is no simple matter. For this reason, MANA is engaged in research aimed at establishing those technologies under the concept that we have named "nanoarchitectonics," which enables creation of new material functionalities by controlling the arrangement and interactions of materials in nano-sized units. MANA is also developing innovative new materials on the basis of nanoarchitectonics in diverse fields, which we hope will result in great advances in the nanotechnology of the 21st century.

1 Oxide nanosheets, new solution to future nanoelectronics

Takayoshi Sasaki (PI), Minoru Osada (PI)

Nanosheets for next-generation electronic devices

As electronics continue to decrease in size, new classes of materials are necessary to continue this downsizing trend. Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness and infinite planar lengths, have been emerging as important new materials due to their unique properties. In particular, the development of exotic 2D systems such as graphene and inorganic nanosheets has provided new possibilities and applications in nanoelectronics.

Among various inorganic nanosheets, oxide nanosheets are important and fascinating research targets because of the innumerable varieties of layered oxide materials with interesting properties such as electrical conductivity, superconductivity, high-κ dielectricity, ferroelectricity, ferromagnetism, etc. MANA is working on the creation of oxide nanosheets and the exploration of their novel functionalities towards applications. For example, MANA discovered high-κ dielectric nanosheets, an important material platform for ultra-small electronic devices, exhibiting the highest permittivity (ε_r = 210~320) ever realized in all known ultrathin (<10 nm) dielectrics.

The world's smallest, highest performance capacitor made from "nano building blocks"

MANA also developed the world's smallest, highest performance capacitor by "nanosheet architectonics."

Capacitors based on dielectric thin films are a key component of electronic devices, where they provide essential functions such as storing electrical charge, and blocking direct current while allowing alternating currents to propagate. Because capacitors are essential in our electronic equipments such as cell phones, personal computers, etc., extensive efforts are directed at the developments of high performance capacitors with smaller size and higher capacitance. But current technology with multi-layered ceramic capacitor (MLCC) has almost reached its limit in terms of materials and processing, which in turn limits the performance that manufacturers can achieve. In response, the researchers have gone to the nanoscale, but "nanocapacitors" are not easy to make.

MANA developed a LEGO-like approach, and applied it to make high-performance ultrathin capacitors. MANA used conductive RuO_2 and dielectric $Ca_2Nb_3O_{10}$ nanosheets as core device components. By using solution-based assembly, MANA created a sandwich consisting of layers of two different types of oxide nanosheets to produce an ultrathin capacitor. The new capacitor has a stable capacitance density (~30μF/cm^2), which is 1,000 times higher than that of currently available commercial products despite the thickness of 30 nm, a 50 times reduction compared to MLCC.

MANA also utilized high-κ dielectric nanosheets as building blocks in the LEGO-like assembly, and successfully developed various functional nanodevices such as field effect transistors, artificial ferroelectrics/

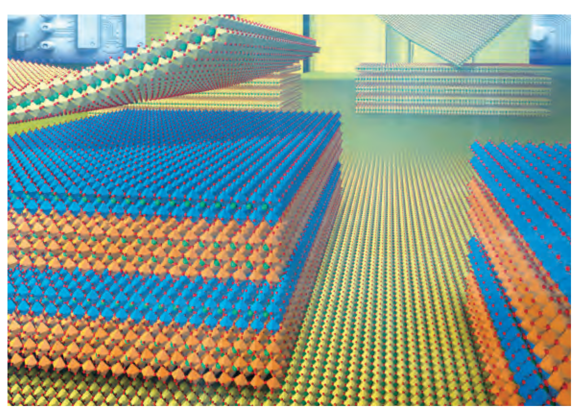


Fig. 1 Image for device fabrication process by nanosheet architectonics. Sophisticated functionalities of nanodevices can be designed through the selection of nanosheets and precisely controlled over their arrangement.

multiferroelectrics, metamaterials, actuator crystals, etc. Our work is a proof-of-concept, showing that new functionalities and nanodevices can be made from "nanosheet architectonics."

M. Osada et al., Advanced Materials, 24, 210, 2012.
C. Wang et al., ACS Nano, 8, 5449, 2014.

2 Atomic switch with synaptic remembering and forgetting operations

Tsuyoshi Hasegawa (PI), Kazuya Terabe (PI), Masakazu Aono (PI)

"Atomic switch" – the world's smallest mechanical switch

An "atomic switch" is a switching device that operates through the transference of metallic atoms/ions and a redox process, which occur when a voltage is applied.

The world's first atomic switch (Fig. 2) was invented by MANA Director Masakazu Aono, et al. The switch has a structure in which a gap of approximately 1 nm exists between the tip of a silver sulfide needle and a platinum surface, which function as electrodes. By controlling the voltage applied to the needle, chemically-reduced silver atoms precipitate in the gap, resulting in contact between the electrodes, and the device is switched "on." The device is switched "off" when oxidized silver ions return to the needle and the gap between the electrodes is reestablished. It requires an extremely small amount of electrical power to start up, and realizes on-off operations depending on whether or not only a few atoms are present in the gap.

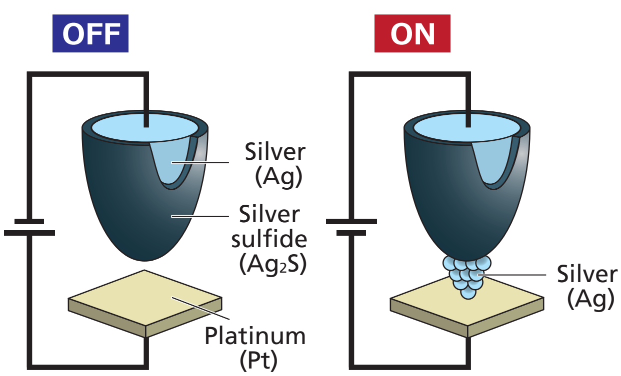


Fig. 2 Schematic diagram of an atomic switch that switches "on" when silver atoms are discharged from a silver sulfide needle.

Realizing synapse elements with atomic switches

MANA researchers are pursuing the world's first demonstration experiment after discovering that the atomic switch operates as a "synaptic element" that autonomously reproduces neural activities in the brain, which are characterized by "remembering necessary information" and "forgetting unnecessary information."

Synapses are junctions that form between the nerve cells (neurons) that make up the neural circuits in living organisms. When the action potential of a neuron reaches a synapse, a neurotransmitter is released and a synaptic potential is generated and transmitted as the action potential of the next neuron. Synaptic connections where this stimulus occurs frequently are strengthened, and as a result, memory is strengthened. In other words, "remembering necessary information" and "forgetting unnecessary information," which are the distinctive features of the brain, are thought to correspond to changes in the strength of synaptic connections.

The atomic switch displays behavior that corresponds closely to these changes in the strength of synaptic connections in the brain. When an electrical signal is input frequently, a stable conducting path (bridge) is created between the electrodes by the efficient precipitation of silver atoms. Conversely, the conducting path disappears over time when the frequency of input is low. Thus, the higher the signal input frequency, the thicker and more stable the bridge becomes (Fig. 3).

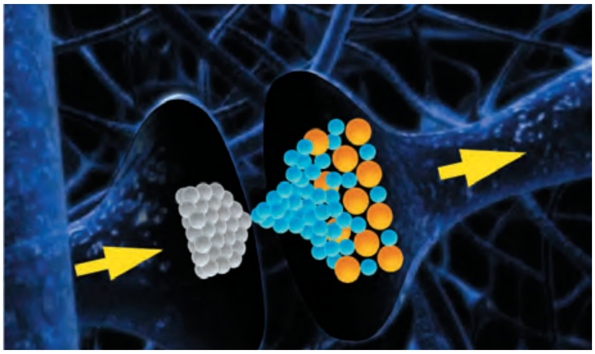


Fig. 3 Schematic diagram of an atomic switch with synaptic operation. When an electrical signal is input, a bridge is formed between the electrodes by precipitation of silver atoms from the electrode on the right.

The road to an artificial brain

Since it has been pointed out that existing computers will not be able to cope with the future demand for higher performance and diversification, attention has been focused on the development of neural circuit/brain-type computers. Artificially reproducing the synaptic functions of brain neural circuits is essentially important, and the synaptic function has already been reproduced by complex circuits and software, however, this approach requires a drive program that has been designed in advance. In contrast, research has shown that circuits that incorporate the synaptic elements developed by MANA can create calculation functions without advance operational design. In the future, progress is expected in research toward the realization of artificial intelligence materials that become more intelligent (learn and grow) with experience.

T. Hasegawa et al., Advanced Materials, 22, 1831, 2010.

T. Ohno et al., Nature Materials, 10, 591, 2011.

3 Development of electron microscope for *in-situ* measurement of nanomaterial functions

Yoshio Bando (PI), Dmitri Golberg (PI)

The difficulty of measuring nanomaterials

In materials science, nanomaterials have attracted the greatest interest over the past several decades. Nano-sized materials display different physical properties than those of the bulk (i.e., those states in which a substance exists in a large quantity to some degree), including mechanical, electrical, thermoelectric, electrochemical, magnetic, piezoelectric, photoelectric, photoelectromotive properties and others. While it is expected to be possible to obtain a variety of functions by combining nanomaterials and various technologies, a precise grasp of the nature of nanomaterials is extremely important in the stage of actual applications.

In measurements of the physical properties of nanomaterials to date, it was possible to investigate the surface form by the scanning electron microscope (SEM), scanning tunneling microscope (STM), atomic force microscope (AFM) and other techniques, but a detailed knowledge of the internal structure was still out of reach. As a result, it was unclear how the measured property data were influenced by nano-level conditions, namely, the shape, the crystal structure, elemental distribution and defect structure of the nanomaterial. In fact, some scientific papers reported very different property data, and this was a serious hurdle to the practical application and industrial use of nanomaterials.

New *in-situ* property measurement instrument

To overcome the hurdles caused by measurement techniques, MANA developed an instrument which makes it possible to manipulate individual nanomaterials while performing observation by high resolution transmission electron microscopy (HRTEM). This enabled *in-situ* measurement of physical properties, which simultaneously captures the changes in properties and changes in the material structure at the nano-level. With this instrument, it is possible to acquire enlarged images with magnification of 2 x 10^6 times and observe deeply into the crystal structure of nanomaterials. In addition to applying voltage, resistance heating, electrostatic charge, bending, tension, peeling, and light irradiation, it is also possible to measure mechanical, electrical, thermal and optical properties while manipulating the sample with nanometer precision. By using an STM probe (for measurement of electrical characteristics), AFM cantilever (for measurement of mechanical properties) and optical fiber (for measure of photoelectric/photovoltaic properties) in combination with the conventional HRTEM specimen holder, the new instrument has made it possible to measure diverse properties of more than 50 different nanomaterials, including nanotubes, nanowires, nanosheets, graphene and nanoparticles.

Toward elucidation of the causal relationship between structure and physical properties

Analysis by the *in-situ* property measurement instrument is innovative, in that it is possible to investigate the physical properties of individual nano-level structures by utilizing its extremely high spatial resolution, temporal resolution and energy resolution, which could be obtained only with HRTEM. As another important attraction, *in-situ* measurements are also possible in real-time, at each step in the structural changes of nanomaterials.

Utilizing this technique, MANA has already realized elastoplastic analysis, measurement of the electron transport property, etc. of nanomaterials, for example, when bending or tension is applied (Fig. 4). In the future, more active use of this *in-situ* property measurement instrument will make it possible to clarify the relationship between the nanostructure and physical properties of nanomaterials and open new

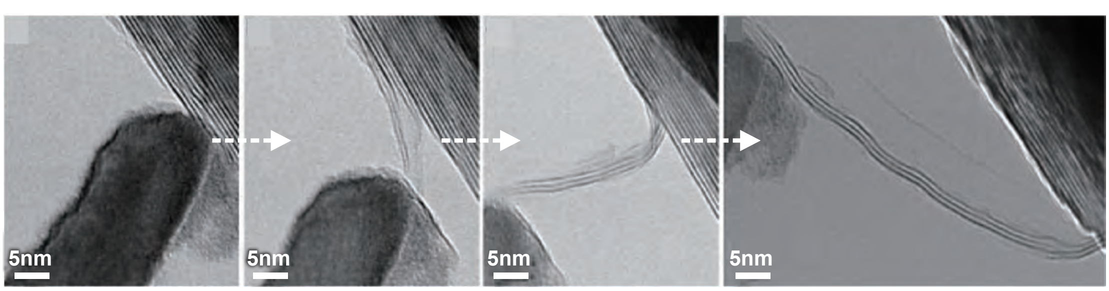


Fig. 4 HRTEM images showing the dynamics of the Scotch tape method of peeling atomic layers. It is possible to peel 3 atomic layers from a layered MoS_2 single crystal by skillfully manipulating the metal probe in the *in-situ* property measurement instrument.

paths in the development of nanomaterial applications.

D. Golberg et al., Advanced Materials, 24, 177, 2012.
D. M. Tang et al., Nature Communication, 5, 3631, 2014.

4 Highly sensitive and compact nanomechanical sensor realizing "mobile olfaction"

Genki Yoshikawa (Group Leader)

Development of a new sensor –"MSS"

Practical application of molecular sensors that can detect and identify various types of molecules has been desired in various fields, including foods, medicine, healthcare, security and the environment science. Nanomechanical sensors, which are one type of molecular sensors, detect surface stress induced by target molecules adsorbed on receptor layers coated on the sensor surface. Nanomechanical sensors can be very versatile because various materials including organic, inorganic and bio molecules can be utilized for receptor layers. However, it was difficult for conventional nanomechanical sensors to satisfy both high sensitivity and compact system, which had been a long-standing challenge for over 20 years. Through the fusion of four basic sciences *i.e.* structural mechanics, materials science, crystallography and electric circuit science, we developed a new nanomechanical sensor called the "Membrane-type Surface stress Sensor (MSS)," which achieved both high sensitivity and compact size. The MSS has a sensitivity more than 100 times higher than that of conventional cantilever-based piezoresistive nanomechanical sensors, and realizes the integration of more than 100 sensor elements in 1 cm^2.

The MSS also possesses a number of other outstanding features: Compatibility with mass production (1$ per chip in future) and integration based on conventional semiconductor microfabrication technology, low power consumption (1 mW or less per sensor element), quick response (response time can be less than a few seconds depending on the conditions) and thermal, electrical and mechanical stability. These practical features of the MSS provide the opportunities for various applications to mobile or IoT devices, contributing to safety and security in daily life in the areas such as freshness/quality control of foods, health management, environmental monitoring and security control.

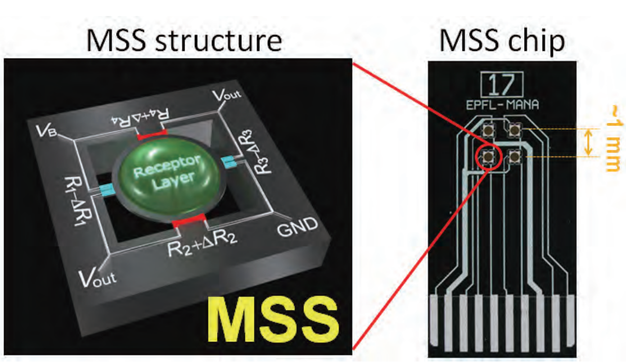


Fig. 5 Left: Schematic illustration of the MSS structure. Surface stress generated by the adsorption of target molecules on the receptor layer is detected electrically with high efficiency by piezoresistors embedded in the four surrounding bridges. Right: Optical microscope image of an MSS chip.

The possibility of a mobile "olfactory sensor"

One of the most important applications of the MSS is an artificial olfactory sensor. We have already demonstrated the identification of various specimens by smell including meat, spices, perfume and beverages. In a joint research between the Swiss Federal Institute of Technology in Lausanne, the University of Basel and MANA, cancer patients were identified through breath analysis using MSS. Research is now underway to explore a variety of applications including reliable cancer diagnosis with small stress to patients, personal diagnosis of daily monitoring of health, and mobile olfactory sensing (Fig. 6).

Fig. 6 Application as a mobile olfactory sensor device for monitoring health conditions by analyzing exhaled breath.

Moves toward practical application and standardization

With the aim of social implementation of MSS as a sensor system, six organizations including NIMS (parent institute of MANA), Kyocera, Osaka University, NEC, Sumitomo Seika and NanoWorld jointly launched an industry-academia-governmental joint research framework called "MSS Alliance" in September 2015. This alliance focuses on the integration of various cutting-edge technologies towards reliable odor analysis system and industrial standardization.

G. Yoshikawa et al., Nano Letters, 11, 1044, 2011.
F. Loizeau et al., Proceedings IEEE MEMS, 26, 621, 2013.

5 Discovery of mechanisms for enhanced performance of thermoelectric materials

Takao Mori (PI)

The importance of development of thermoelectric materials and related issues

Only about 1/3 of the primary energy (petroleum, coal, gas, etc.) used by humankind is effectively utilized, and most of the remainder is simply lost as waste heat. For this reason, high expectations are placed on solid-state thermoelectric material devices which convert waste heat directly into useful electricity by using the phenomenon called the Seebeck effect, whereby a temperature difference is converted to voltage.

At present, thermoelectric devices have not reached wide practical application due to the inadequate performance of the thermoelectric materials. To begin with, in power generation by thermoelectric materials, it is necessary to create a temperature differential in the material, and also to extract electric current. However, it is generally difficult to realize a condition in which current flows but heat does not, i.e., maintaining the temperature differential, and thereby, achieving high performance in a thermoelectric material. As an additional challenge, the main components of conventional high performance thermoelectric materials are scarce, expensive and/or toxic elements such as bismuth (Bi), tellurium (Te), lead (Pb), silver (Ag), hafnium (Hf), etc.

Therefore, MANA is pioneering the mechanisms for achieving high functionality in compounds of elements that are more abundant in nature in order to contribute to wide-ranging practical application of thermoelectric materials.

Nanoarchitectonics of thermoelectric materials

Focusing on the difference in the mean free paths of phonons and charge carriers, suppressing thermal conduction may be realized by more selective scattering of phonons. In recent years, this method has enjoyed worldwide popularity for achieving high thermoelectric performance. Because the design of a proper nanostructure is the key for the success of this idea, MANA established a nanoarchitectonics approach in which nanosheets of thermoelectric materials are synthesized and utilized, resulting in improved thermoelectric performance.

This is a simple method that uses little energy, and is expected to be applicable to a wider range of thermoelectric materials in the future. Furthermore, dramatically improved performance can be expected if nanosheets can be assembled in a high-order structure designed by nanoarchitectonics (Fig. 7).

The search for new principles

The nanostructuring of thermoelectric materials is a powerful method for achieving high thermoelectric performance. It is also extremely important to discover new principles for improving the figure of merit, which expresses the performance of thermoelectric materials. MANA discovered that $CuFeS_2$ shows high thermoelectric performance even at around room temperature. Toxicity is not a problem with the component elements of this material, namely, copper (Cu), iron (Fe) and sulfur (S), and the material itself exists in abundance in nature in the form of a copper iron sulfide mineral called chalcopyrite. The magnetism of the material can be adjusted by controlling the content of Fe, and MANA research has shown that it is possible to improve thermoelectric performance by appropriate adjustment of the coupling of the charge carriers and magnons (Fig. 8). (A magnon is a quasiparticle related to the oscillations of the magnetic moment of electrons in a magnetic body.)

C. Nethravathi, et al., Journal of Materials Chemistry A, 2, 985, 2014.

R. Ang et al., Angewandte Chemie, 54, 12909, 2015.

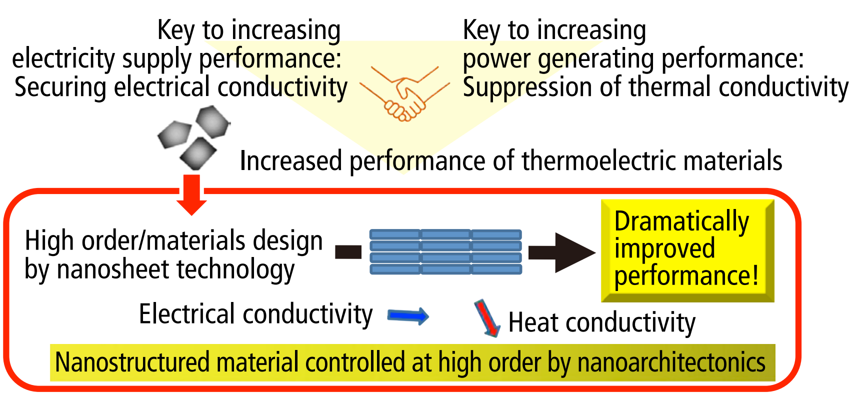


Fig. 7 Realization of high thermoelectric performance by utilizing nanostructures. Securing electrical conductivity and suppressing heat conductivity are achieved simultaneously through nanoarchitectonics utilizing nanosheet technology, and a dramatic improvement of thermoelectric performance is achieved.

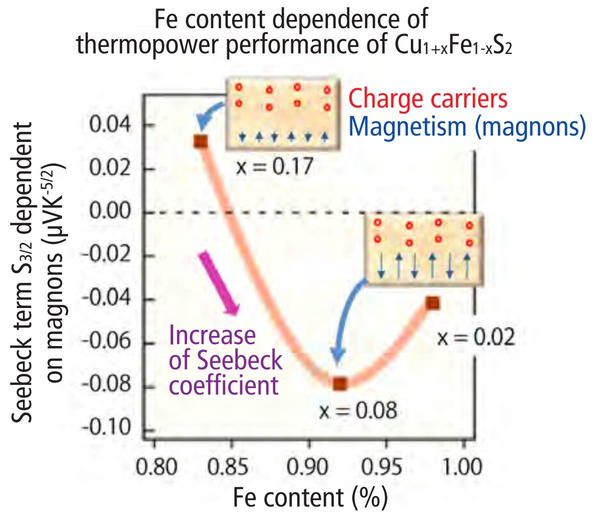
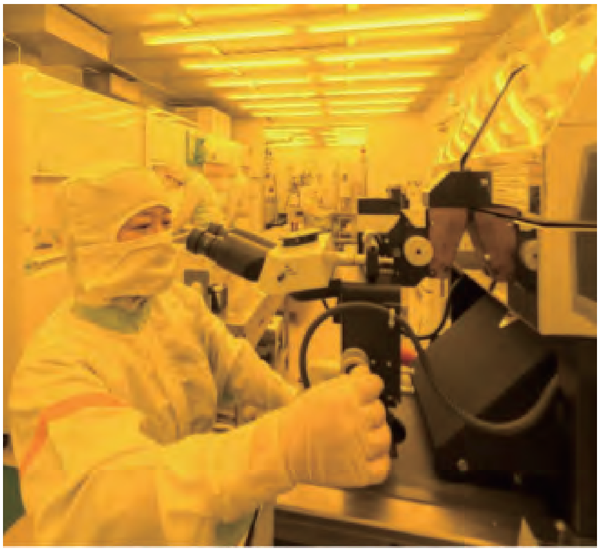


Fig. 8 Change of thermopower performance (change of Seebeck term $S_{3/2}$) when the coupling contributions of charge carriers and magnons are adjusted by controlling the iron content of the magnetic semiconductor $Cu_{1+x}Fe_{1-x}S_2$. In this figure, the optimum coupling is realized and improvement of thermopower performance is observed at x=0.08.



Young researchers who have come to MANA from around the world cooperating in an experiment in a cleanroom

MANA to date, and outlook for the future

MANA grew into a world-class research institute in the field of nanotechnology with the support of the WPI program (WPI: World Premiere International Research Center Initiative). This is also proof that the missions of WPI were indeed on target. One of the missions of the WPI is "Fusion." Basic research begins with individual research and frequently advances to high level research as a result of the formation of a group of researchers or a "trend" of research. MANA additionally gave birth to "dynamic research" that produces world-class research results by encouraging a fusion of research activities, ideas and concepts which are already at a high level. The mission of the WPI also includes "Globalization." In this respect as well, MANA has demonstrated a fusion effect, in the form of a high level of research, by introducing different cultures and thinking in a front-line research center in Japan, thereby creating a new research environment. While the five outstanding research achievements described above are all results of such fusion effects, MANA has also cultivating a large number of other germinal ideas for research.

From the outset, MANA realized that the fusion and globalization would not progress by simply gathering researchers from different fields and from different countries. Before the WPI program, the National Research Institute for Materials Science (NIMS), with the support of Japan's Ministry of Education, Culture, Sports, Science & Technology (MEXT), had operated the International Center for Young Scientists (ICYS). The ICYS established a system for accepting and fostering outstanding young scientists from around the world and accumulated experience in coping with the "culture shock" that accompanies internationalization. Based on that experience, MANA has become the most globalized international research center in Japan by conducting various unique programs that encourage globalization and fusion under the auspices of WPI. As one result, in terms of the level of its research results, MANA now ranks with the top research institutes in other countries such as Harvard University and MIT. At present, half of the researchers working at MANA are non-Japanese. MANA is continuing to promote cutting-edge research through cooperation among young researchers who have gathered here from Japan, other Asian countries, Europe, USA and Oceania.

MANA is also extremely active in collaboration with overseas research institutes, and the international network of nanotechnology research centered on MANA is growing steadily. As just one example, more than 250 young scientists who gained experience at MANA are now spreading their wings in countries throughout the world.

At MANA, this successful experience is deeply engraved in our hearts. In achieving unique and high level of research results as one of the world's top research centers, MANA learned that dynamic operation of a research center is necessary and indispensable for realizing fusion and globalization. While continuing to spread this essence of MANA to NIMS as a whole, and to all of Japan, we also intend to play an active role as a "catalyst hub" for nanotechnology research by bringing together the best scientific brains from around the world.

Tomonobu Nakayama (MANA)