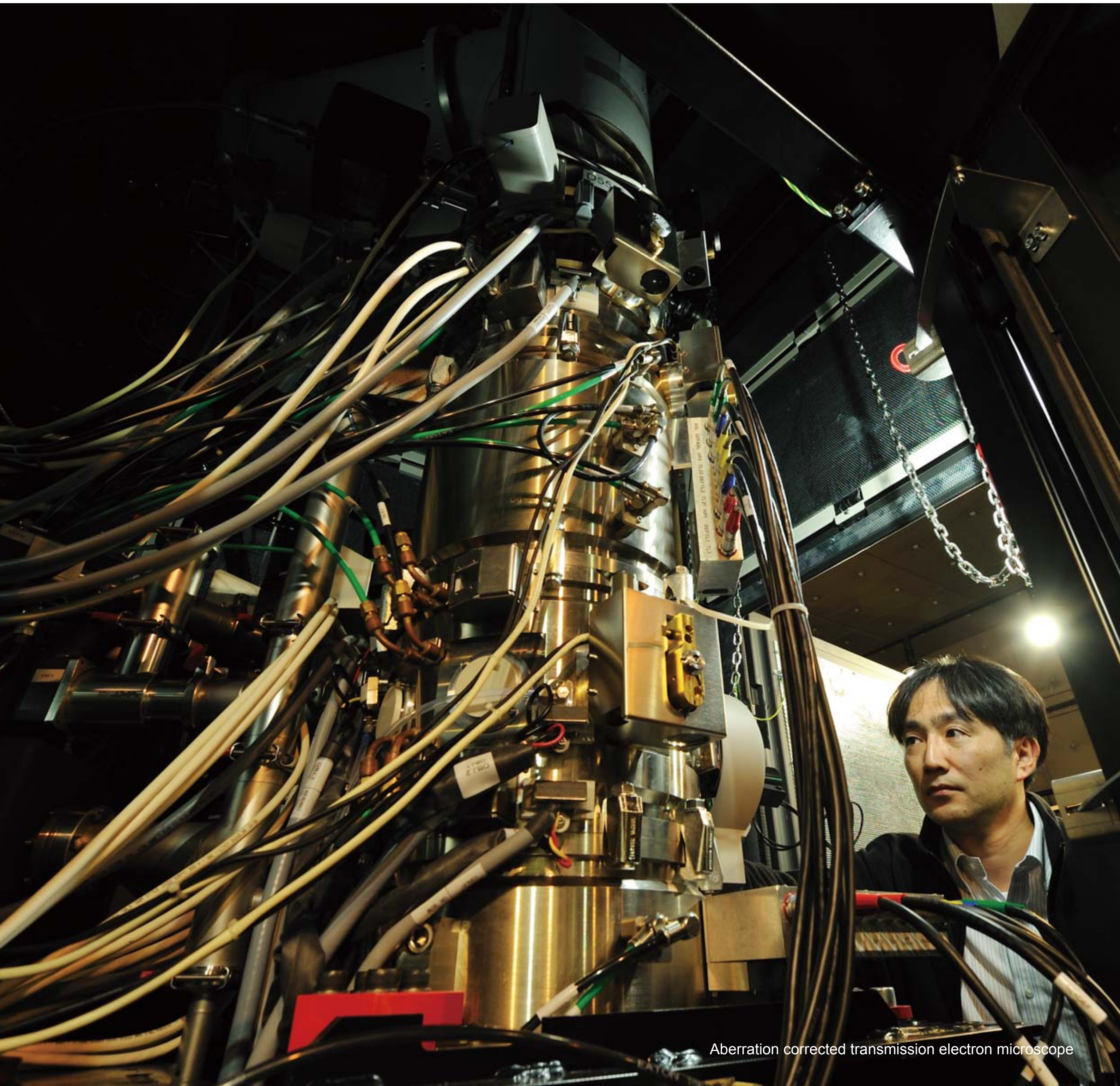
NIMS NOW
International

2011. January

Materials Innovation by Advanced Nano Characterization Technologies



Aberration corrected transmission electron microscope

New Year’s Greetings from the President

Prof. Sukekatsu Ushioda
President of NIMS

Happy New Year!

All of us at NIMS realize the importance of our mission as members of the core national laboratory for materials science, and as before we will work coherently and cooperatively toward our goal.

We start the third “Intermediate-range Plan” (2011-2015) in April as the second term ends in March. During the past year we have been formulating the new “Intermediate-range Plan.” At the same time, the national government is also in the process of deciding the “Fourth Basic Science and Technology Policy” (2011-2015). In the “Third Basic Science and Technology Policy” the government specified the science and technology areas that should be emphasized as the basis for the prosperity of our society. In contrast, the “Fourth Basic Science and Technology Policy” will be “outcome oriented.” That is, the new Policy will first define the social needs that require solutions and then decide the science and technology areas that need strengthening.

Two years ago, we set up the “Center of Nanomaterials Science for Environment and Energy.” This Center is indeed carrying out “outcome oriented” research. The outcome expected of this Center is the solution of energy and environmental problems through technological breakthroughs in photovoltaic cells, secondary batteries, fuel cells, and photocatalysts. This will be accomplished by close integration of theory and computational simulation, and through “open innovation” processes participated by many experts in the country. The objectives of this Center are in line with the national policy for “green innovation” for economic growth. Last year we set up another center aimed at environmental issues. This is the “Hub for Low Carbon Emission Network.” Currently we are constructing an environmentally efficient building to house these Centers “under one roof.”

Toward the end of last year, a sudden stoppage of rare metal exportation by the Chinese government made people focus on the importance of rare metals to our industry. NIMS had been conducting research on the supply and effective use of rare metals. This year we will accelerate our research on the development of substitute materials and recycling technology of rare metals. We call this, “Strategic Research on Atomic Elements.” It is an important part of NIMS’s mission as a core national laboratory to expeditiously meet the challenges that endanger our industries.

The level of our science and technology cannot be raised or even maintained by concentrating only on research oriented toward specific outcomes. We must at the same time continue to support curiosity-driven research whose outcome is not clear. NIMS will continue to invest sufficient resources and efforts to curiosity-driven research along with the outcome-oriented research.

NIMS wishes to be a research institute that can meet the rapidly changing social needs flexibly and dynamically. For this purpose, all of our staff must have the ability and will to adapt their expertise toward directions required by the nation. We will endeavor to dynamically utilize our human resources and research funds.

I would like to ask our friends to give us continued support this New Year as in the past, and at the same time wish them the best in the New Year.

Advanced Nano Characterization Accelerating Various Research

NIMS boasts a wide variety of advanced characterization devices.
Many of these were developed independently by NIMS researchers themselves.
Why?
Using advanced technologies, it is possible to observe objects which had not been visible until now,
and measure objects which could not be measured in the past.
With these technologies, researchers know where they are now,
and can advance into the next unknown areas.
The driving force which will carry materials research from the present into the future – the advanced nano characterization technologies and researchers at NIMS.

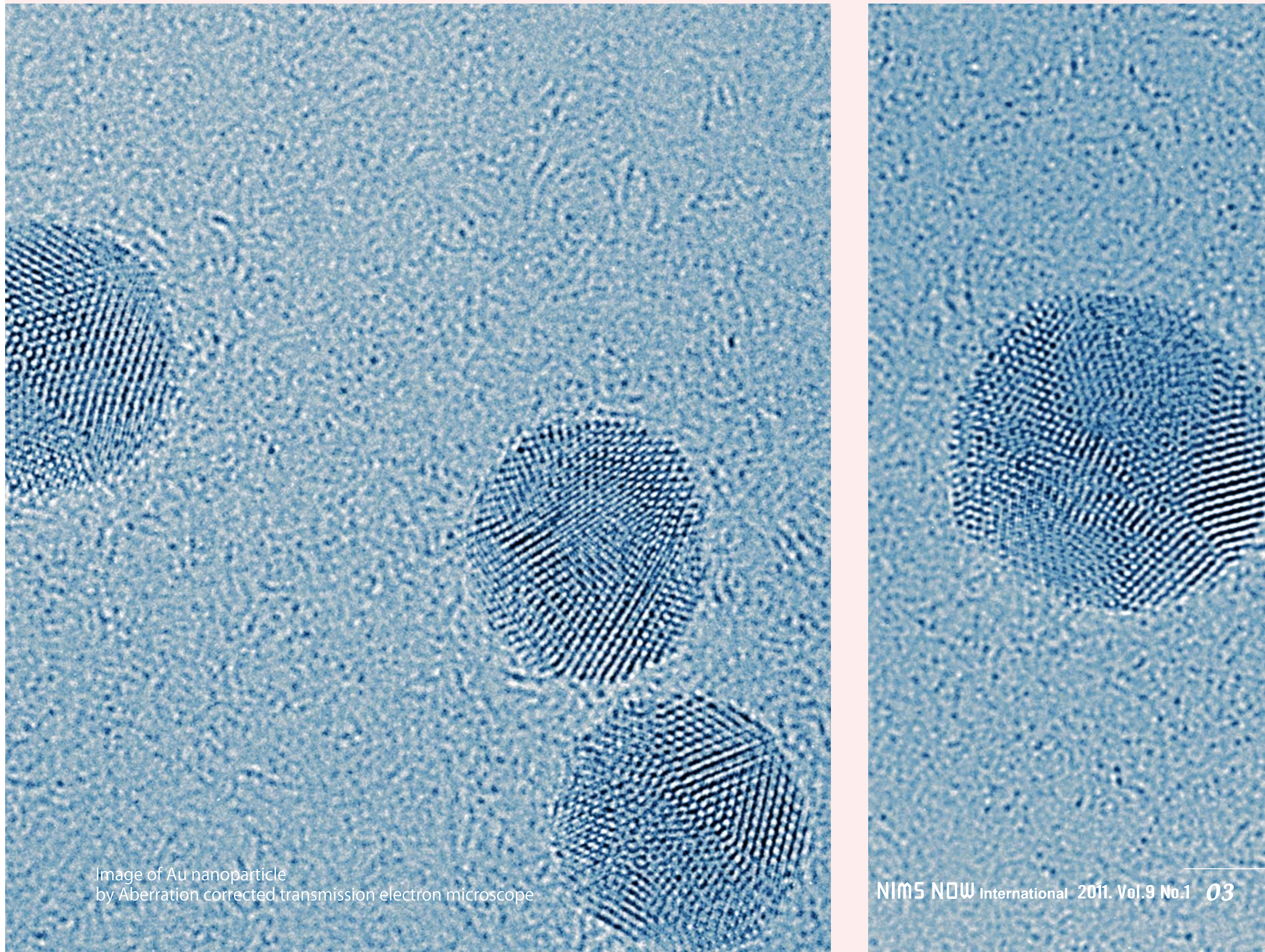


Image of Au nanoparticle
by Aberration corrected transmission electron microscope

Materials Innovation by Advanced Nano Characterization Technologies

Daisuke Fujita
Managing Director,
Advanced Nano Characterization Center

The growing importance of characterization technologies.

As a country which depends on foreign sources for natural resources and energy, Japan's strategy is to be an innovation-oriented nation based on advanced science and technology. In the Science and Technology Strategy of Japan, "Nanotechnology area: Advanced characterization/fabrication technologies" was selected as one concrete challenge for accelerating the creation of innovation based on "True Nano*" and innovative materials technologies, and constructing the infrastructure for ensuring superiority in international competition. On the other hand, there is also an increasing recognition of the importance of characterization technologies in other countries. For example, the United States has declared that knowledge obtained by measurement is key for continuing progress in technology, innovation, and guaranteeing the economic security of the country, highlighting the importance of the role of measurement in innovation.

Toward advanced nano characterization responding to the needs of materials science and technology.

Because nano characterization technologies which respond to diverse needs related to materials are indispensible for accelerating innovation, it is imperative that NIMS lead the way in advanced nano characterization technologies of the world's highest level. Our aim is to establish advanced nano characterization technologies which are capable of elucidating the elemental composition of materials, their shapes and atomic structures, and the properties and functions which they possess.

Today's materials science is continuing to evolve toward a scientific system based on measurement at the nanoscale and modeling using theoretical calculations. Supporting this, imaging measurement with spatial resolution at the atomic level to nanoscale, and high level spectroscopy capable of identifying bonding states and electronic states at the single atom level are demanded.

Furthermore, the creation and functions of materials have their origins in diverse interactions with environmental fields. For this reason, measurement in environmental fields related to the creation and functions of specific materials is essential. This type of measurement is called in situ measurement, from the Latin meaning "in the essential location." For materials, the goal is nano level measurement while realizing the "environment in which the material essentially exists," and analysis of the mechanism responsible for the creation and functions of the material.

Promoting advanced nano characterization.

The mission of the NIMS Advanced Nano Characterization Center, which was established in 2006, is to develop advanced nano characterization technologies which contribute to fundamental and infrastructural research on new and advanced materials, and to contribute to material innovation by applying those technologies to advanced materials. Our objective is to develop comprehensive advanced characterization technologies for amorphous and single crystals, and surface/near-surface layer to solid interfaces, and to supply techniques and data which are useful in materials research at the nanoscale.

We are promoting advanced nano characterization with scanning probe microscopy (SPM) under extreme fields for nano creation and function search, ultra-high resolution, high sensitivity transmission electron microscopy (TEM), high resolution solid-state nuclear magnetic resonance (NMR) utilizing high magnetic fields, femtosecond ultrafast time-resolved analysis and measurement, wide area and near-surface layer 3-dimensional nano analytical technology, etc. based on the core competence technologies of NIMS.

Daisuke Fujita, Dr. Eng. Obtained master's degree in the Department of Metallurgy and Materials Science, Graduate School of Engineering, the University of Tokyo. After serving as a research associate in the Institute of Industrial Science, the University of Tokyo, and as a researcher at the National Research Institute for Metals (NRIM; now NIMS), now Coordinating Director of the Key Nanotechnologies Field at NIMS.

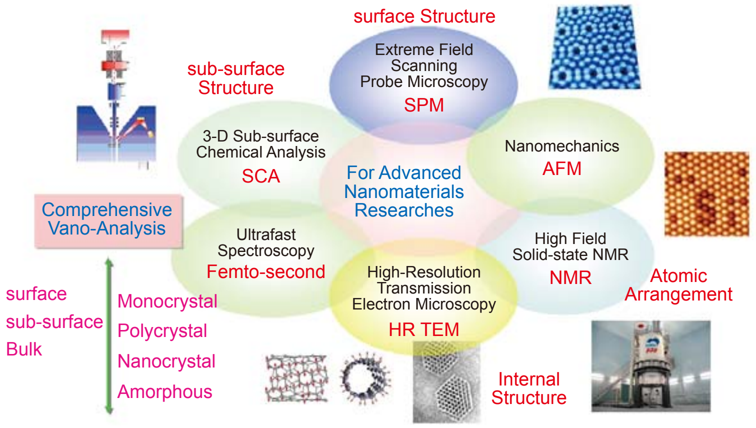


Fig. Development of key advanced nano characterization technologies of the world's highest standard, including surface, near-surface, and the interior of solids.

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* **True Nano:** Means research and development which is not limited simply to observation and is not an extension of conventional work, but takes advantage of the features of nanotechnology to create new fields of industry.

Development of Advanced Electron Microscopy Techniques and Application to Material Characterization

Koji Kimoto
Group Leader
Advanced Electron Microscopy Group,
Advanced Nano Characterization Center

The importance of material characterization using electron microscopy.

The unique physical properties and outstanding features of advanced materials depend on the crystal structure and additives of microscopic regions of the material. It can be said that the micro parts of materials determine their macro properties. For this reason, transmission electron microscopy (TEM), which makes it possible to observe microscopic regions, has become a necessary and indispensable tool for materials development.

The NIMS Advanced Electron Microscopy Group is engaged in research from the viewpoint of development and improvement of electron microscopy characterization techniques and their application to various types of materials. Although the electron microscope was invented about 80 years ago, new technical development is continuing even today. In particular, a variety of new techniques which were developed in the last decade have made it possible to observe and analyze materials at the atomic level. At present, researchers are continuing to develop and improve new characterization techniques.

Recent research achievements at NIMS.

Here, we will introduce just a few examples of recent research by the Advanced Electron Microscopy Group. These are (a) development of a specimen scanning-type confocal electron microscope (**Fig. 1**),[1,2] (b) visualization of atomic column/dopant by scanning transmission electron microscopy (STEM; **Fig. 2**),[3,4] and (c) development of a high energy resolution X-ray detector for TEM using a microcalorimeter (**Fig. 3**).[5]

The aim of the research with the confocal electron microscope is to realize 3-dimensional observation, with the STEM instrument is to realize high sensitivity and high accuracy, and with the microcalorimeter is to achieve an improved elemental identification capacity.

The group is also engaged in observation of magnetic domain structures using Lorentz microscopy. Three-dimensional observation can be applied to catalytic materials, in which a large number of small particles are dispersed, while high resolution, high sensitivity measurement is applicable to the characterization of semiconductor devices and metallic materials, and observation of magnetic domains can be used in characterization of spintronics devices. More detailed explanations of these techniques can be found in the papers by the respective authors and at the group's website.

Future research.

In the future, the development of environmental and energy-related materials will become increasingly important. To answer this need, the Advanced Electron Microscopy Group will expand the techniques which it has developed to date to the characterization of those materials, and will also improve techniques to meet the special requirements of the various objects of measurement.

Aiming at new advances in characterization techniques, we have begun research on a type of electron microscopy which will make it possible to analyze individual atoms. We have also begun research using some of the world's most advanced TEM instruments, including a device which converges electrons to the size of an atom by aberration correction, and a monochromator which selects incident electrons with uniform energy.

Koji Kimoto, Dr. Sci. Obtained doctoral degree at Tohoku University. Before joining NIMS, worked as a researcher at the Hitachi Research Laboratory, Hitachi, Ltd. Joined the National Institute for Research in Inorganic Materials (NIRIM; now NIMS) in 1999. Present position since 2010. Also a Professor of the Graduate School of Engineering, Kyushu University.

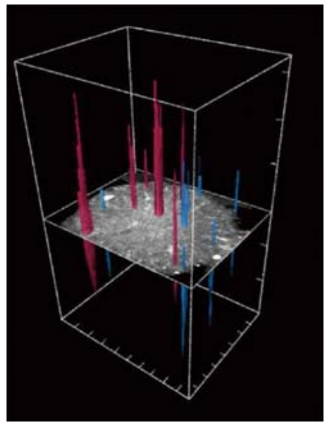

Fig.1 Example of observation by specimen scanning-type confocal electron microscope.

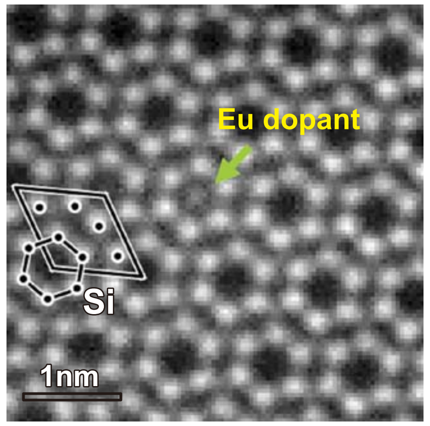

Fig.2 Example of observation of Eu dopant in β-SiAlON.

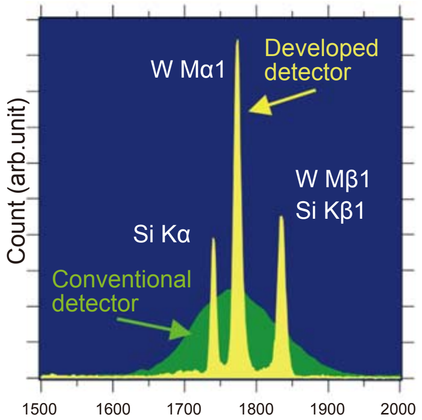

Fig.3 Results of measurement with microcalorimeter.

References
1) A. Hashimoto, et al. J. Appl. Phys. 106 (2009) 0861011.
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3) K. Kimoto, et al., Nature 450 (2007) 702.
4) K. Kimoto, et al., Appl. Phys. Lett. 94 (2009) 041908.
5) T. Hara et al., J. Electron Microsc. 59(2010) 17.
http://www.nims.go.jp/AEMG/index-j.html
http://www.nims.go.jp/hvems/AEMG_sakura/

Nanoprobe Characterization for Materials Research

Daisuke Fujita
Goup Leader,
Advanced Scanning Probe Microscopy Group
Managing Director,
Advanced Nano Characterization Center

Features of nanoprobe techniques using SPM.

Innovative materials, exemplified by materials used in nanoelectronics and photovoltaic cells, are a driving force for realizing a sustainable, advanced information society. With these materials, there is a high possibility of utilizing material functions that result from extremely small size, such as surface effects and quantum effects, and nanoscale analytical techniques for this purpose are desired.

Scanning probe microscopy (SPM) is a type of nanoprobe measurement which makes it possible to analyze the structure, physical properties, and functions of the surfaces of materials by scanning a probe with a nanoscale sharpened tip, and is sensitive to the outermost surface. As a feature of nanoprobe technology using SPM, while being a characterization technique, this technology also has nanoscale material creation/fabrication functions. SPM is a technique for measuring surface/interfacial structures with atomic resolution, and at the same time, it can also be used as a technique for fabrication (lithography), creation (dot growth), and manipulation (atomic manipulation) of surfaces and interfaces at the nanoscale.

Newly-required environment-controlled nanoprobe techniques.

In conventional practice, nano measurements were performed in the unique "measurement environment" of the measuring device. On the other hand, environmental and energy materials manifest their functions in diverse environmental fields. For example, researchers in solar power generation and photocatalytic materials require measurements which contribute to elucidating the structure and mechanism responsible for the manifestation of functions in controlled light-irradiation fields.

Thus, from the standpoint of developing materials at the nanoscale, (1) fusion of creation and measurement and (2) measurement in the environment in which the material manifests its functions are required. Furthermore, because needs are not limited to surface/interfacial structure and shape, but also include clarification of physical properties and functions, (3) multidimensionality of measurement functions is also required. "Multidimensionality of measurement functions" means measurement of multiple types of information characterizing the functions and physical properties of materials from the same object.

As a nano characterization technology which answers these requirements, we are developing "surface multifunctional nanoprobe technology in controlled fields (environment-controlled nanoprobe technology)." With environment-controlled nanoprobe technology, our aim is to realize measurement using, as the measurement space, an environment which is close to the creation or use environment or the field in which functions and properties are manifest. This will contribute to elucidating the mechanism by which materials are created and manifest functions (**Fig.**).

An engine for standardization of nanoprobe characterization technology.

In order to ensure the social acceptance of nanomaterials, verification of the safety of nano products is indispensable. To achieve this, quantitative measurement of nanomaterials is essential, and the ability to compare results is necessary. Thus, establishment of standards based on international agreement is also desired in the field of nanoprobe measurement.

Pre-standardization research to improve the quantifiability of nanoprobe measurements and reliable measurement methods is indispensable. As mid- to long-term efforts in accordance with an international scheme are necessary, we are also playing a role in leading standardization of nanoprobe characterization technology.

Profile is on P4.

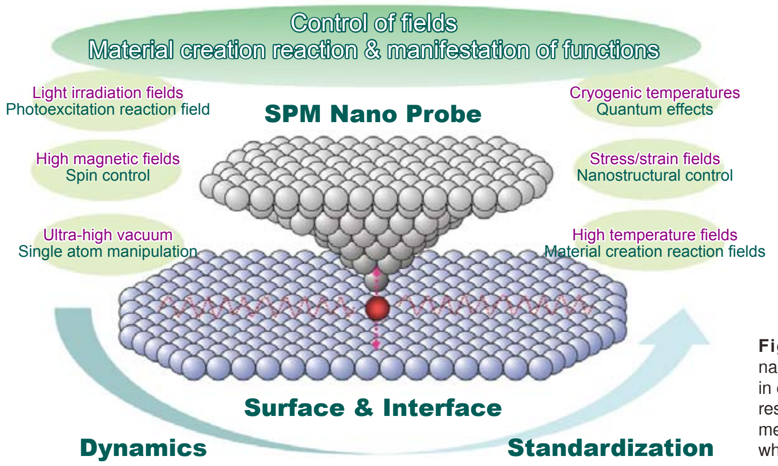

Fig. Foundation of materials research utilizing nanotechnology = "Surface nanoprobe measurement in controlled environments." Our aim is to realize high resolution/multifunctional nano analysis in the environments in which materials are created/environments in which functions are manifest.

Angle-Resolved Reflection Electron Energy Loss Spectrum

Hideki Yoshikawa
Advanced Surface Chemical Analysis Group,
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Hua Jin
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Materials Analysis Station,
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Making database library for the dielectric response functions of materials.

The precise evaluation of electron inelastic mean free path and inelastic scattering background is indispensable in the quantitative analysis of electron spectra. These basic physical quantities are derived by the information on the dielectric response of materials. Noted that the cutting-edge quantitative analysis needs the electron transport simulator based on these physical quantities. Normally, the dielectric response function or the energy loss function (ELF) is obtained from optical absorption/reflection measurements. However, in the optical measurements, a large-scale synchrotron radiation facility is necessary because a light source with variable wavelength (10-1000eV) from the low energy vacuum ultraviolet (VUV) region to the soft X-ray region is required. For this reason, small numbers of materials have been measured, and for the majority of materials, no optical data are available especially in the energy range of 10-50eV where electron excitation of the valence band is dominant.

Therefore, in order to obtain the ELFs and optical constants for various materials in a simple manner, without the use of synchrotron radiation or other large-scale facilities, we developed a technique for obtaining these values from the angle-resolved reflection electron energy loss spectra (REELS). The precise angle-resolved measurements are performed using an inclined specimen-holder rotation method developed at NIMS, and the optical ELF is determined by the factor analysis of angle-resolved REELS data. It is also possible to obtain the optical constant from the obtained ELF. The utility of this method has been demonstrated by application to Si and SiO_2 specimens (**Fig. 1**).

Demonstration with compound semiconductors and future applications.

In spite of the great importance of the various compound semiconductors, beginning with gallium nitride (GaN), no data of their optical constants or ELFs exist at 10-50eV. Therefore, using the developed method, we performed measurements of the ELFs of gallium arsenide (GaAs). The results are shown in **Fig. 2**.

First, in order to remove the surface contamination and oxide layers of the GaAs specimen, the cleaning treatment was performed by two methods:removal of oxidized layer by deoxidized water or by ion beam sputtering. While holding the GaAs specimens at a constant electron incident angle, the angle-resolved REELS was measured at 3000, 4000, and 4500eV while varying the electron take-off angle from 15° to 75° by rotating the inclined specimen holder.

As a result of measurements of these specimens, we found that specimens, which received different cleaning treatments and have different residual damaged layer,showed good agreement of ELF values. Therefore, it can be concluded that ELF data of the non-damaged deep layer is evaluated by separating the contributions of the damaged surface layer and the non-damaged deeper layer. Furthermore, these ELFs also showed good agreement with our first-principles calculation result. From this demonstration, it can be understood that the developed method is applicable to the evaluation of a wide variety of materials with the simple specimen pre-treatment.

In the future, we plan to obtain dielectric functions of the group III-V and II-VI semiconductors, for which optical constants were not measured so far, and construct and open a database of both experimental results and theoretical calculations.

Hideki Yoshikawa, Dr. Eng.Completed doctoral course at the Osaka University Graduate School of Engineering in 1992. JSPS Fellow (1992-1993). Served as a Researcher at the NEC Fundamental Research Laboratories (1993-1995), and the NIRIM (1995-2001). Became NIMS Researcher when NIRIM was reorganized in 2001.
Hua Jin, Ph.D. Obtained Ph.D. at Chungbuk National University (Korea) in 2006. Lecturer at Harbin Institute of Technology in China (2007-2008). Postdoctoral researcher at NIMS Advanced Nano Characterization Center (2008-2010).
Hideo Iwai, Dr. Sci. Obtained Dr. Sci. at the Ritsumeikan University in 1999 and was employed at Ulvac-Phi, Inc. until 2007. Joined NIMS as a Research Fellow in 2007 and joined Materials Analysis Station in 2009.
Shigeo Tanuma, Dr. Sci. Completed the doctoral course at the University of Tsukuba Graduate School in 1982 and joined Nippon Mining (later reorganized as Japan Energy Corporation) in the same year. Visiting Researcher at the NBS (now NIST) 1985-1987. Joined NIMS in 2001.

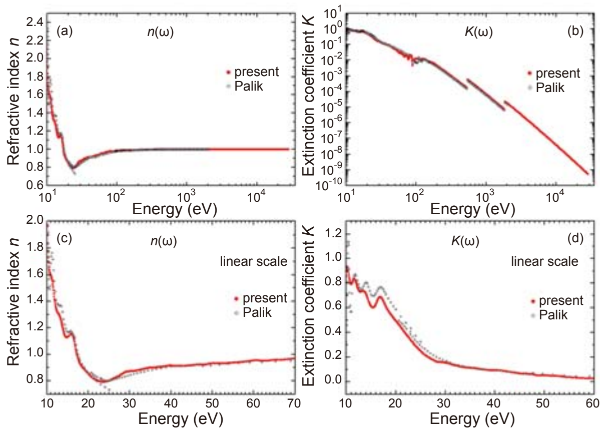


Fig.1 Optical constants of SiO_2 specimens. Red dots show the results of this research, and white circles are results from the reference.

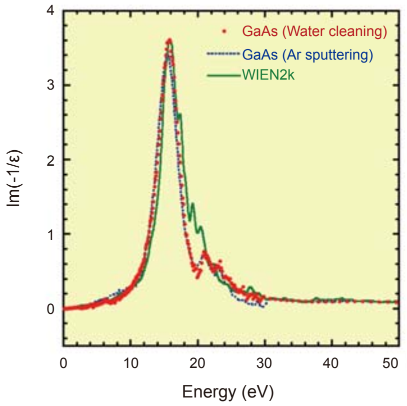


Fig.2 Optical energy loss function of GaAs. The red dots and blue dotted line are the results of this research, and the solid line shows the values obtained by the first-principles calculations.

Development of High-sensitivity Ultrafast Spectroscopy and its Application to Photonic Materials Fabrication

Kunie Ishioka
Ultrafast Spectroscopy Group,
Advanced Nano Characterization Center

Timescale of microscopic processes determines photonic efficiency.

In our daily life, we are surrounded by photonic materials, which work as photocatalysts, solar cells, light emitting diodes (LEDs), lasers, etc. The optical functions are associated with microscopic processes such as photo-excitation of electron-hole pairs, their energy-relaxation, transport, and radiative recombinations. The efficiency of the photonic materials often relies on the time scales — typically between femtosecond (10^{-15} s) and microsecond (10^{-6} s) — of the competing microscopic processes.

We study the ultrafast optical response of the photonic materials such as semiconductors and their nanostructures by using a pump-probe technique. By combining a pair of matched photodetectors with fast scan of pump-probe delay or lock-in detection, we achieve high sensitivity in reflectivity or transmission measurements as small as <10^{-5}. This enables us to monitor the photonic materials and devices under weak light illumination, in conditions close to the “practical” operation.

Femtosecond optical pulses to assist materials development.

Femtosecond optical pulses induce coherent phonons in the materials, through which we can monitor the collective atomic motions in the real time and extract information on the time-dependent electron-phonon coupling. Sub 10fs ultrashort optical pulses can excite high-frequency phonons such as the in-plane C-C stretching (also called G mode) of graphite (**Fig. 1**). The frequency of the coherent in-plane phonon upshifts with increasing excitation density. Time-resolved analysis reveals that the frequency upshifts instantaneously at the photoexcitation, and then relaxes to the stationary value in picosecond time scale (**Fig. 2**). We have revealed that this light-induced frequency upshift is due to the "non-adiabatic" effect that is characteristic to the quasi-2D electronic structure of graphite.

NIMS is actively involved in research on photonic materials, ranging from photovoltaic cells to photocatalysts to LEDs. We are aiming to provide feedback to these researches from the viewpoint of optical physics and promote their development with our state-of-the-art ultrafast spectroscopy techniques.

Kunie Ishioka, Dr. Sci. Obtained doctoral degree from the Graduate School of Science, Kyoto University in 1994, and joined NRIM in the same year. Visiting Researcher at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in 1998-1999. Present position since 2006.

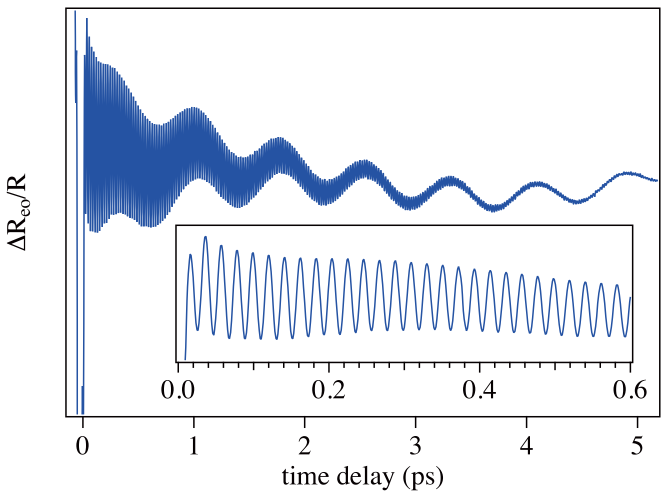


Fig.1 Transient reflectivity change of graphite (HOPG) measured by the pump-probe technique using sub-10fs optical pulses. Periodic modulations due to coherent in-plane C-C stretching (period of 21fs) and interplanar shear vibration (770fs) are observed.

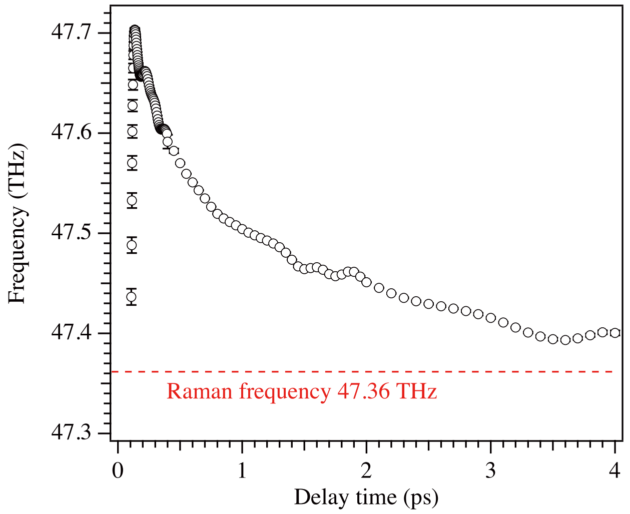


Fig.2 Time evolution of the G mode frequency of graphite after femtosecond optical pulse excitation. The upshift immediately after the photoexcitation is due to the breakdown of the Born-Oppenheimer approximation, in which the photodoped carriers cannot follow the in-plane C-C stretching. The frequency recovers to the unexcited value as the photoexcited carriers relax.

Development of High Field Solid-State NMR and Application to Materials Analysis

Tadashi Shimizu
Group Leader
High Field NMR Group,
Advanced Nano Characterization Center

To expand the range of applications of NMR.

Conventional nuclear magnetic resonance (NMR) could only demonstrate a tiny part of the true capabilities which NMR intrinsically possesses. Although NMR can theoretically be applied to approximately 80 of the elements of the periodic table, due to technical constraints, the objects of research with NMR had conventionally been limited to only a few elements, such as hydrogen, with which its sensitivity and resolution are particularly useful. As a result, only some research fields, such as organic molecules, could enjoy the advantages of NMR.

The most effective technique for expanding the range of applications of NMR is use of a high magnetic field. While common-type NMR uses a 10T class magnetic field, if a field exceeding 20T can be applied, NMR can be applied for the first time to the most difficult elements, which are called the quadrupolar nuclei elements (the nucleus having a nuclear spin quantum number I ≧1). These elements occupy approximately 60% of the periodic table. With conventional NMR, extremely low resolution with the quadrupolar nuclei elements had been an issue, and in principle, the only method of solving this problem is use of a high field. If precise measurements of quadrupolar nuclei can be realized by using high field solid-state NMR, NMR can be expected to contribute to a wide range of material fields, including inorganic materials. In particular, because NMR is comparatively effective in the analysis of non-crystalline structures, it can be expected to play a complementary role to conventional techniques such as X-ray and electron microscopy.

World’s first successful high-resolution measurement of practical materials such as Ca, Mg, Ti, and Mo.

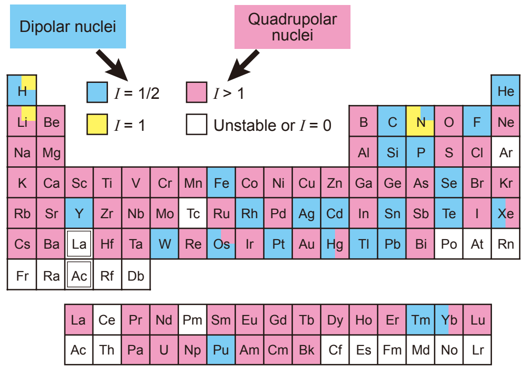
Fig. 1 is a graph showing the relative difficulty of observation of the quadrupolar nuclei. The contour lines in this figure show that higher magnetic fields are necessary in order to analyze elements with higher degrees of difficulty (lower right in the figure). The red circles indicate quadrupolar nuclei which NIMS has succeeded in observing during the past 5 year using the 930MHz-NMR instrument (magnetic field strength: 21.8T) currently in operation at NIMS.

In particular, it is noteworthy that we have succeeded in high resolution measurements of various practical materials for the first time in the world, including Ca, Mg, Ti, Mo, and others with the highest degree of difficulty. These are all elements with which signals were completely invisible with the conventional instruments using a 10T class field. Furthermore, even when we say that signals are “visible,” this does not mean that the signals are visible to the eye from the start; they finally become visible after integration for more than 100 hours. During the first several days of the experiment, we patiently continued the task of narrowing down the measurement conditions, which consisted of about 20 types of parameters. This work was supported by high level specialized knowledge and expert skills, which adjusted “virtual signals” with the mind’s eye.

Solid-state NMR of quadrupolar nuclei is a technique which was made possible by the realization of >20T magnets and is still in its infancy. Because virtually no past materials or literature exists, we are still finding our way in the dark. Nevertheless, we have a real feeling of the pleasure of exploring a new field. Our aim is to overcome the preconceived idea that NMR is a device which is only suitable for organic chemistry and expand the range of observation using solid-state NMR to diverse materials.

Tadashi Shimizu, Dr. Sci. Assistant Researcher at The University of Tokyo, Institute for Solid State Physics from 1987. Joined NRIM in 1990, and current position from 2001.

Table.1 The sensitivity and resolution of the dipole nuclei (blue) is proportional to the magnetic field. The sensitivity and resolution of the quadrupolar nuclei (red and yellow) increases by the 2nd to 5th power of the field. Because a field of 20T or more is necessary in order to obtain high resolution, these elements are outside the range of analysis by conventional NMR (magnetic field of around 10T).



Dipolar nuclei
Quadrupolar nuclei

🟦 I = 1/2
🟨 I = 1
🟥 I > 1
☐ Unstable or I = 0

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db													

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

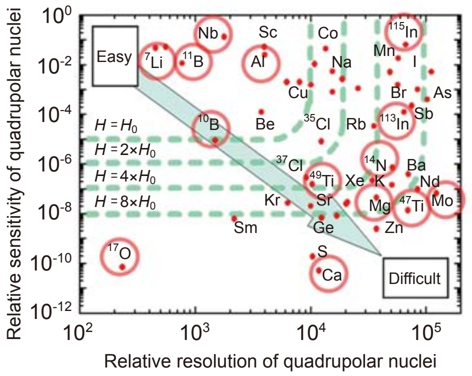


Fig.1 Graph showing the relative difficulty of NMR measurement of quadrupolar nuclei. The contour lines (blue dotted lines) show that the possibility of observation increases with higher magnetic fields. The red circles are examples of results with quadrupolar nuclei, in which NIMS actually succeeded in observation of practical materials using its 930MHz NMR instrument.

Characterization Techniques Enable Us to Achieve the Unknown Information

Professor Yoshimasa Nihei

Special Adviser, Tokyo University of Science

Professor Nihei has been involved in research since the dawn of instrumental analytical chemistry. He has devoted his career to the search for and establishment of the advanced concepts of techniques in analytical chemistry, as well as actual analytical techniques. Because the measurement and analysis technology is the origin of scientific and technological capabilities, we asked Prof. Nihei how NIMS can contribute to this field.

— You have continually stressed the importance of measurement and characterization techniques for progress in science and technology.

I belong to the third generation of researchers in industrial analytical chemistry. The first generation is represented by Prof. Takayuki Somiya, who won the Japan Academy Prize for analysis of hydrogen in steel. Prof. Somiya developed many practical analysis methods for iron and steel, beginning with precision analysis of the composition of gas in these materials, and contributed to raising the Japanese iron and steel industry to the world's top level. I was led to do surface analysis by Prof. Hitoshi Kamada, who belonged to the second generation. This was already 40 years ago. Prof. Kamada was the most important leader in the establishment of the analytical equipment industry in Japan, and later received the Japan Academy Prize for "Development and Application of High Sensitivity Analytical Instruments," which also included my surface analysis method.

However, my starting point at that time was the debate about the significance of quantitative analysis of surfaces. For materials development, it was necessary to perform analyses by probing only a thin layer of the surface. One method was analysis of the velocity of electrons ejected from the surface using X-ray technology. This was truly a nanometer order job.

— This was a forerunner of today's nanotechnology.

It was certainly at the nano order. The principle was developed by Swedish physicist who won the Nobel Prize(*1). I stress that characterization techniques are the starting point for science and technology because, while Japan has an ample ability to produce devices, we do little original research and development in the field of analytical instruments. In other words, the importance of "acquiring unknown information which nobody knows" is not adequately understood by researchers in various fields. It is generally said that "Researchers in Japan have lost the memory of the genesis of science." In the period when original Japanese advanced analytical devices were finally beginning to appear, the Japanese government of the mid-80s inaugurated a "Buy American" policy, and Japan's analytical equipment industry lost its vitality. After that, Europe and the United States swept the field, and now, the only top-level technologies that are left are electron microscopes, nano-measurement semiconductor inspection devices, and similar items.

— China can catch up with Japan in this area?

Yes. I insisted that Japan must also create and expand national projects for this, but this long-cherished desire wasn't fulfilled. Fortunately, a new project was launched, occasioned by the award of the Nobel Prize to Koichi Tanaka(*2), and this is now in its 7th year.

— And the results are still to come . . .

Verification of the principle doesn't require a lot of time, but the creation of a usable device as merchandize takes around 10 years. Of course, several examples of success have already appeared, and the ultra-sensitive high-resolution mass spectrometry developed by our project will be used in near future in analysis of the microparticles returned to earth by the asteroid exploration vehicle "Hayabusa".

— I suppose this is an area which is difficult for the private sector, and we must inevitably turn to the public sector?

Once characterization devices are completed, they are extremely useful, but until that time, the risk is large. For this reason, even in the United States, this type of work depends on funding from the national government, though prototypes are created by ventures. Since NIMS is operated with government funding, and also has the staff and equipment, I hope that you will be a driving force for Japan as a whole. I believe that making great account of the measurement of the nano region up to now was an appropriate judgment. On the other hand, going forward, it will probably be necessary to devote attention to the life sciences field. Because this is the field where advanced measurement and analysis is most needed.

— Do you have any comments on young students in Japan?

It is too slow to think about what specialty they want to go into and what laboratory they want to join, after they entered university. Comparing Japan and the United States, although Japanese students have higher academic ability when they start university, how they study after entering university is completely different. American students set their own goals and then race toward them. As a result, the tables are completely turned by the time students reach graduate school. Americans spend enough time playing when they are children. In this process, they discover what they want to do in the future, and they study intensely after they enter university. I hope that young Japanese students will do at least as much.

Yoshimasa Nihei, Dr. Eng. Graduated from the Faculty of Engineering, University of Tokyo, and also held positions as Lecturer, Associate Professor, and Professor at the same univ. Appointed as a Professor of Tokyo University of Science in 2001 and has his present position since 2006. Has been involved in industrial analytical chemistry and research on devices for surface science, etc. during this period.

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*1 Kai Siegbahn received the Nobel Prize in Physics in 1981 for "developing the method of Electron Spectroscopy for Chemical Analysis (ESCA)."
*2 Koichi Tanaka was a co-recipient of the Nobel Prize in 2002 for "development of a method for identification and structural analysis of biological macromolecules."

Development of Next Generation LaB_6 Electron Source for Electron Microscopes

Jie Tang
Group Leader
1D Nanomaterials Group,
Exploratory Materials Research Laboratory for Reliability and Safety

Han Zhang
ICYS Researcher

To improve the resolution of electron microscopes, the development of an electron source which emits bright and finely focused point electron beam is necessary. The performance of an electron source depends on the emission material and the method of electron emission. Lanthanum hexaboride (LaB_6), which emits electrons at a comparatively low extraction voltage, is the optimum electron source material, and the field emission method, in which electrons are emitted utilizing only an electrical field, is the optimum electron emission method.

However, LaB_6 is difficult to process at the nano level due to its high hardness. As a result, it had not been possible to develop a needle-like electron source, which would enable easy emission of electrons using only an electrical field, and only the conventional method, in which heating was used to extract electrons, was used.

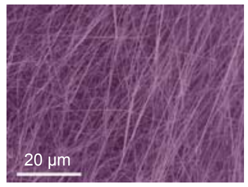


Fig.1 Example of the formed LaB_6 single crystalline nanowires.

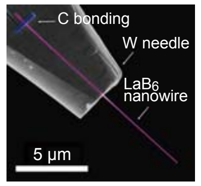


Fig.2 Electron beam source fabricated by joining a LaB_6 nanowire to a tungsten (W) needle holder.

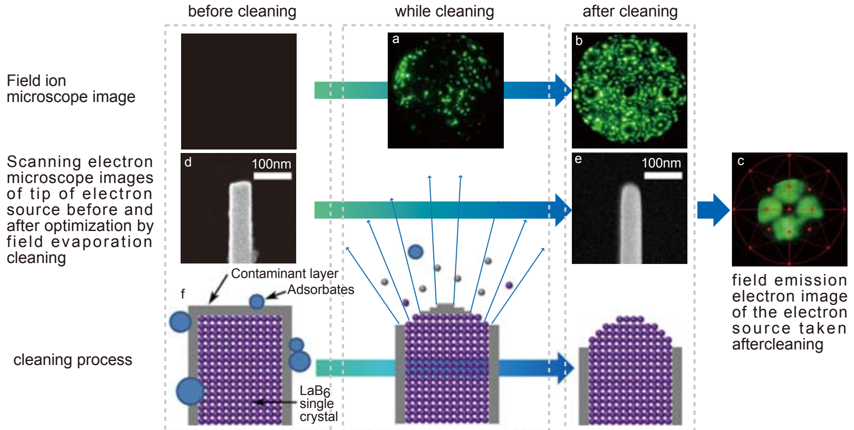


Fig.3 (a, b) Field ion microscope images in which clear image in (b) was obtained by field evaporation cleaning of the surface of the LaB6 single crystalline nanowire electron source, (c) a field emission electron image of the electron source, (d, e) scanning electron microscope images of the tip of the electron source before and after optimization by field evaporation cleaning, and (f) a schematic illustration showing the cleaning process.

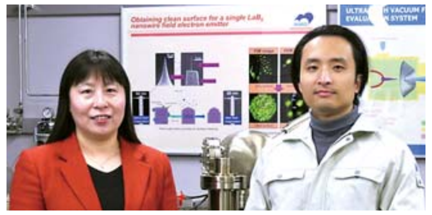
In collaboration with Professor Lu-Chang Qin of the University of North Carolina at Chapel Hill (USA), using a high temperature chemical vapor deposition technique, this NIMS group succeeded for the first time in the world in synthesis and growth of fine single crystalline nanowires of LaB_6 with diameters of 20-200 nm and lengths of several 10-50 μm on a substrate, as shown in **Fig. 1**. As can be understood from **Fig. 1**, a large number of nanowires with a uniform nano-level diameter have grown to a considerable length.

An individual single crystalline nanowire was selected and arranged onto a tungsten needle, and carbon was then bonded to the nanowire by vapor deposition (**Fig. 2**). This is the heart of the LaB_6 point electron source. Using a 50 nm diameter LaB_6 electron source, it is possible to emit a bright, finely focused electron beam simply by applying a voltage without heating.

Fig. 3 shows various images when a voltage of 3 kV was applied to this electron source in a field ion microscope and the surface of the nanowire was cleaned by field evaporation, together with a schematic diagram of this process. In this field evaporation process, contaminant atoms at the surface of the electron source were desorbed using a high electrical field, and the surface was cleaned. As shown in **Fig. 3b**, the atomic image produced by the field ion microscope became sharp and crisp. **Fig. 3c** is a field emission electron image obtained from this electron source. The tip of the electron source was sharpened by the field evaporation technique (**Fig. 3d** and **3e**), and the adsorbed atoms, surface contaminants, and corner parts which cause unnecessary field emission were removed (**Fig. 3f**). Thus, this research provided an experimental demonstration that the method of cleaning by field evaporation not only results in emission of a high-brightness electron beam from the crystal plane which is suited to generation of the electron beam, but also greatly reduces deterioration of the electron source in operation.

Continuing on this work, the group is conducting a detailed investigation of the properties of the developed LaB_6 single crystalline nanowire field emission electron source. In comparison with LaB_6 thermionic electron sources and the tungsten field emission electron sources, which currently offers the highest performance, the newly-developed field emission electron source displays extremely high performance, including a brightness (of the electron beam) more than ten times greater. For example, if this electron source is used as an electron gun for a transmission electron microscope, the resolution of the electron microscope will be greatly improved, and the world's highest resolution can be expected.

The NIMS group is continuing with research and development aiming at practical applications to enable incorporation of this new electron source in analytical instruments involving electron beams, such as electron microscopes and electron beam lithography devices, and improvement of their performance.

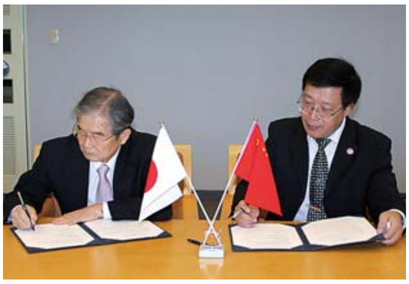


Jie Tang, Ph.D. (left) Joined NRIM in April 1993. NIMS Senior Researcher and Group Leader of the 1D Nanomaterials Group. Also, concurrently teaches in the Joint Doctoral Program in Materials Science and Engineering, University of Tsukuba and holds a concurrent position as Adjunct Professor of the University of North Carolina at Chapel Hill (US).

Han Zhang, Ph.D. (right) After obtaining doctoral degree from the University of North Carolina at Chapel Hill, joined NIMS as a Postdoctoral Fellow. Also worked as a Fellow of the Japan Society for the Promotion of Science. Has been NIMS ICYS Researcher since 2010.

NIMS New Partnership

On December 20, 2010, NIMS signed a Comprehensive Collaborative Agreement (a sister institute agreement) with Xi'an Jiaotong University (XJTU), which is one of the oldest universities in China, founded in 1896 initially at Shanghai and later moved to Xi'an. XJTU is one of the government's most intensively invested universities and there are about 1,200 faculty members with doctoral degree, 13,000 postgraduate and 17,000 undergraduate students. XJTU has produced many scholars like professors at University of Cambridge and University of Oxford. NIMS has been collaborating with XJTU through many activities such as MOU, Joint Graduate School and annual joint workshops. This agreement would not only reinforce the existing collaboration but also envisage new collaboration and exchange of researchers in much broader field.



NIMS President Prof. Ushioda (left) and XJTU Vice-President Prof. Song (right) at the signing ceremony

Mr. Lim Chaun Poh, Chairman of Singapore's Agency for Science, Technology and Research, Visits NIMS

On December 15, 2010, Mr. Lim Chaun Poh, Chairman of the Republic of Singapore's Agency for Science, Technology and Research (A*STAR) visited NIMS. Mr. Poh had informal talks with NIMS President Sukekatsu Ushioda and Vice-President Tetsuji Noda, including an exchange of views on the science and technology policies of the two countries and cooperation between NIMS and the National University of Singapore (NUS) and Singapore's Institute of Materials Research and Engineering (IMRE).

Mr. Poh has also served as a member of the World Premier International Research Institute (WPI) Initiative Evaluation Committee. After talks with President Ushioda and Vice-President Noda, he observed the International Center for Materials Nanoarchitectonics (MANA), which is a NIMS project under the WPI Program. During his visit to MANA, Mr. Poh received an explanation of the Center's work from MANA's Director-General, Masakazu Aono, listened with keen interest as MANA Principal Investigators described research achievements in the fields of solid-state fuel cell materials, atomic switches, and nanotubes, and actively discussed various issues with MANA researchers.

MANA Principal Investigator Dr. Traversa (left) explaining his research to Mr. Poh (right)

Hello from NIMS

He Shaoxin and Salvatore Grasso in Sanya island (China)

Salvatore Grasso (Italy)

Ph.D. Student / Nano Ceramic Center
Since Apr. 2007

Hello dear friends,

My name is Letizia Grasso, I'm 7 months old. I was born in Italy, and I have spent 5 months in Tsukuba with my mum and my dad. I'm not so sure, I think my dad is doing something at NIMS (the building in front of my bedroom), which I don't really understand. He always comes back home and talks about nano and he says that nanotechnology will make the world better. My dad looks at me and says that I'm the best sample he has ever made. My mum is so wonderful, she is taking care so much of our lovely family. All my family is so busy in taking care of me, they offer me 24 hours 5 stars service which includes feeding, cleaning, washing, bathing, singing, dancing, playing and hug. Nowadays I cannot speak much so I just tell you da da da da da…

Letizia Grasso

National Institute for Materials Science
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