NIMS 6
Research Accomplishments

The 6 key Reseach Accomplishments in FY 2007

SENGEN

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National Institute for Materials Science
http://www.nims.go.jp/eng/index.html

Major Research Accomplishments at NIMS

(On Documentation of Six Major Research Accomplishments in FY2007)

Teruo Kishi, President
Independent Administrative Institution
National Institute for Materials Science
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The research and development of materials whose structure is controlled down to the size of nano-meter is the key to the realization of "sustainable society" in 21st Century by solving the problems in energy and environment. We (NIMS), are carrying out the fundamental research and generic/infrastructural technology research, making efforts to popularize research results, facilitating common use, and fostering researchers and engineers.

For the self-evaluation of research results at NIMS, we have summarized the results, selecting 21 themes in the first period (FY2001 ~ FY2005) and 8 themes in FY2006. In the same manner, we have selected 6 themes for the results in FY2007, and would like to present the research contents to you.

For the sake of innovative development of materials, various kinds of consistent efforts are necessary, including creation of intellectual knowledge on innovative materials, combination of the knowledge, cross-cultural unification of different fields to realize practical use of the knowledge, and further, examination of good and evil which the innovation brings to the society (through harmony of wisdom between social and natural sciences). The fusion of these "intellectual knowledge", "cross-cultural unification of different fields", and "wisdom in social and natural sciences" is the direction of progress which we have to follow in the development of materials. We base ourselves on it in the innovation of materials.

The six research accomplishments which we have selected this year include a wide range of themes, from the ones in the stage of basics/germination to the ones a part of which is already in the application phase as materials. For deeper understanding of the research accomplishments, we attached "explanation of the research field". We hope it will be helpful in understanding the world most-advanced trend of the research field and a little deeper specialty.

Providing infrastructural assistance for research and fostering of researchers are also important mission for NIMS. We present here topics from the start of NIMS Center for Nanotechnology Network and from MANA (Materials Nano-architectonics) which has been selected as one of the World Premier International Research Center Initiative.

Technology development has an important meaning as the starting point for innovation. NIMS is promoting a wide range of researches from those in the stage of germination to project researches, always checking whether we maintain the best management system, in order to advance securely the research and development activities in materials leading to innovation.

Fortunately, in Japan, we have accumulation of superior research and development in materials. It is important, from national strategic points of view, to further the researches on new materials and to harvest the fruits, on the basis of a firm research infrastructure. For the research and development of materials, it is also important to have accumulation of knowledge on the basis of a long term view point and stable research environment. Therefore, it is very important to have a wide support as a national project and to advance researches steadily.

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1. Element-Selective Visualization of Atomic Arrangement in Crystal

The Point of the Research

We have succeeded in visualizing atomic arrangement in a crystal by each element, by using STEM (Scanning Transmission Electron Microscopy) and EELS (Electron Energy-Loss Spectroscopy). By focusing the electron beam as small as diameter of an atom with a highly stabilized apparatus and by detecting electrons scattered by inner-shell electrons, we have succeeded for the first time in discriminatorily observing them with a high spatial resolution[1,2,] .

Contents of the Research

Material Characterization in Nanometer Region Getting More Important

Specific or useful properties of advanced materials are often yielded by crystallographic structure in the region of nanometer. It is already possible to observe crystal structures directly with an advanced electron microscope (*e.g.*, a high-voltage electron microscope), but the image obtained by the conventional electron microscope is basically a “black-and-white” image whose contrast depends on the atomic number, and it was difficult to discriminate the element for each atomic position, namely to make the image “colored” for the discrimination.

Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS)

The technique employed in this research, in which STEM and EELS are combined (Fig. 1), was proposed by Colliex *et al.*, in the 80’s; details of the research development is found in his commentary (Nature **450** (2007) 622). Basic principle is rather simple: A small electron beam is focused on the specimen, and the electron energy-loss spectrum of transmitted electron is acquired with varying the electron beam position. Since energy-loss spectrum shows element-dependent peaks, whose energy depends on inner shells (K, L, M, N …) of each element, we can get two-dimensional elemental distribution with high spatial-resolution.

The Point in This Research

Recent advanced electron microscopes allow us to focus an electron beam in the size of an atomic diameter (*e.g.*, 0.1nm). For characterization of the sample at each atom’s position, however, the following physical conditions are required, and these are our research issues.

There is the problem of degradation in spatial resolution (delocalization) due to incident electron’s behavior inside the crystal (*i.e.*, propagation and scattering). For some crystal structures, it is known that the incident electron gets away from the atomic array where electron beam is focused on[2]. In such a case, visualization of the atomic image is difficult in principle. In addition, the degree of delocalization depends on the energy level of the inner shells, whose electrons are excited when the incident electrons interact with atoms. Simply stated, by exciting electrons deep in energy level (inner shells, close to the nucleus), the information can be localized at the atomic position. NIMS has been engaged in TEM and EELS for many years and continued studying on the delocalization in the case of inelastic scattering[3]. Thanks to recent technical developments, such as remodeling of the apparatus and improvement in stability[4], we have succeeded in obtaining element-distribution images from which atomic arrangement can be discerned[1].

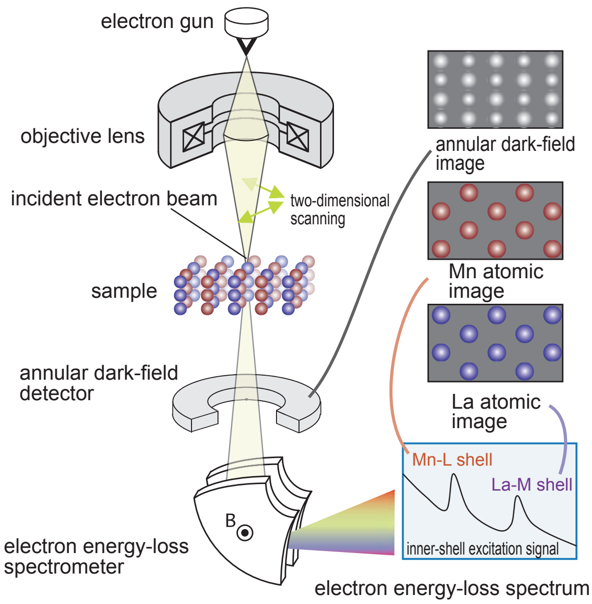


Fig. 1 Schematic drawing of Scanning Transmission Electron Microscopy (STEM) and Electron Energy-Loss Spectroscopy (EELS)
In STEM, electrons, which are focused to the size of an atom (*e.g.*, 0.1nm) and which are penetrated through atomic columns, are used. In EELS, element-specific signals from inner-shell excitation are used to distinguish the element.

Electron Microscopy to Distinguish Atomic Arrangement

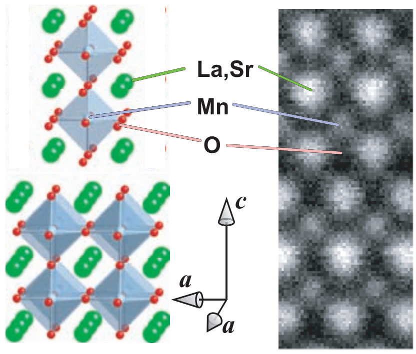
■ Major results

Visualization of Atomic Arrangement for Layered Manganese Oxide[1)]

The layered perovskite compound $(La,Sr)_3Mn_2O_7$, one of ceramics of strongly-correlated electron system which shows peculiar solid-state properties, was observed (The sample was given by Prof. Tokura of the University of Tokyo). In the annular dark-field images, atoms with a large atomic number like lanthanum are observed as bright spots, whereas manganese atoms are observed as slightly bright spots. The elemental identification of ADF images is however not perfect, and there exists other problem that oxygen atoms are invisible. Since only gray scale information is available in ADF images, it is difficult to distinguish elements.

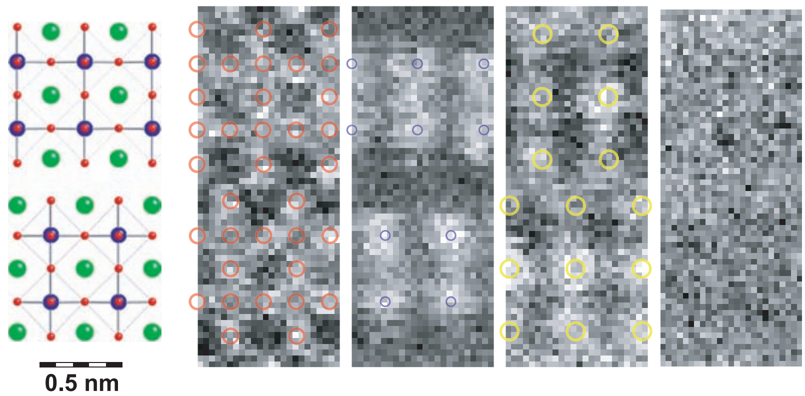
Fig 3 shows visualization of atomic arrangement by each element, which was made possible with our technique. We can see that oxygen atoms (b) and manganese atoms (c) are bright only at the corresponding atomic columns. As for lanthanum atoms, atomic columns are visible for M-shell excited electrons (d), but invisible for outer N-shell excited electrons (e). This is due to the delocalization in inelastic scattering; note that the N-shell electron is outer and low energy-loss in comparison with those of the M-shell.

By using this analytical method, it becomes possible to study such matters as localized structures of the atomic order that causes complex solid-state properties in materials like ceramics of strongly-correlated electron system.



(a) Model of crystal structure (b) Annular dark-field image

Fig. 2 (a) Model of crystal structure and (b) an example of the conventional annular dark-field image



(a) Projected structural model (b) Oxygen map (c) Manganese map (d) Lanthanum map (M-shell excitation) (e) Lanthanum map (N-shell excitation)

Fig.3 Models of projected crystal structure and examples of visualization by each element

Published Research Papers

1) K. Kimoto, T. Asaka, T. Nagai, M. Saito, Y. Matsui and K. Ishizuka: Nature **450**(2007) 702.
2) K. Kimoto, K. Ishizuka and Y. Matsui: Micron **39**(2008) 257.
3) K. Kimoto and Y. Matsui: Ultramicrosc. **96**(2003) 335.
4) K. Kimoto, K. Nakamura, S. Aizawa, S. Isakozawa, Y. Matsui: J. Electron Microsc. **56**(2007) 17.

Expected Innovation

By developing this research, since it can visualize crystal structures down to each element, knowledge can be obtained which directly couples to material characteristics and to properties of materials. This technique is also valuable in analyzing interface of different materials and local defects of the material; it is expected, for example, that this may be applied to the evaluation of various semiconductor devices and magnetic materials.

INQUIRIES

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Microscopy Technology Visualizing Atomic Columns
Technology Developed and Application to Other Materials

We have succeeded in visualizing atomic columns in a crystal by each element using Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS). A part of the result was announced on Nature[1)] and on domestic newspapers[2)]. Here, we review technical contents of the apparatus[3)] and recent research progress.

The Progress of the Research

We have carried out high spatial-resolution analyses using TEM and EELS since the 90's, which have yielded results on element analyses and analyses of chemical bonding with spatial resolution in the order of nanometer[4)]. In order to achieve higher spatial-resolution, STEM-EELS has to be employed from the viewpoint of chromatic aberration of the objective lens and delocalization in the inelastic scattering. We, at NIMS, have been engaged in the research on advanced electron microscopy for a long time as one of the infrastructural technologies for materials researches. As for this research, we have been improved/developed the STEM equipment, and related software since around 2003. In order to analyze elements by every position of the atoms, the following are necessary: (i)the electron beam on the sample has to be focused to the size smaller than inter-atomic distance, (ii) an ultra-high stability has to be realized in order for the incident electrons to stay on an atom, (iii) and to make the incident electrons localize at the position of the atom throughout the process of their propagation in the crystal (iv) and the process of their inelastic scattering . The technical details were described elsewhere1,5). Here, the stability issues, which are related to the technical ones, will be explained.

Fig.1 Photo of STEM

Development of STEM Apparatus with High Stability[3)]

One of the technological barriers against the improvement in spatial accuracy of the analysis position is the disturbance in equipment environments. In the equipment environments, all of the following constitute the disturbance; change of the room temperature or the atmospheric pressure, acoustic/electrical noises, vibration of the floor, and electro-magnetic waves. Our apparatus (Fig. 1), with countermeasures tried to improve stability after trial and error, has become different (including its appearance) from the commercial one (Fig. 2 shows examples before and after the countermeasures tried). To reduce effects of vibration from a road, the apparatus was set up in the vibration-free laboratory in Namiki Site of NIMS. Typical sample drift rate was found to be less than 0.2 nm/min, which was about 1/10 of that for the former apparatus.

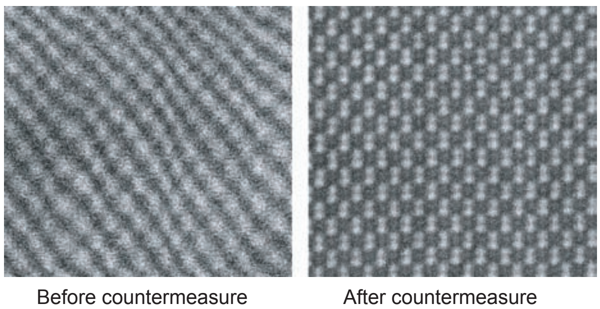


Fig. 2 Annular dark-field images before and after the countermeasure against external disturbance (samples are both Si(110) thin films)

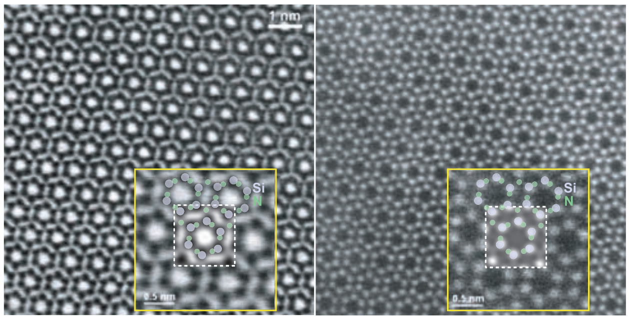
Application to Silicon Nitride Compounds used for Fluorescent Materials

Examples of observation of β- Si_3N_4 crystals, the material which is drawing attention as the fluorescent material for white LED, are shown in Fig. 3. (The specimen was prepared by Dr. Hirosaki of Nano Ceramics Center, NIMS) In the bright-field image, which corresponds to the conventional electron microscope image, the atom position is observed basically as a dark dot; on the other hand, in the annular dark-field image the atom position looks bright. Measurement of one picture frame requires about a minute, but no big distortion is observed in the picture, suggesting a high stability of the apparatus. As on the previous page, Fig.4 shows an example of visualized atomic columns of Si. These STEM images were employed as the cover figures of scientific Journals (Journal of Electron Microscopy, Oxford University Press and Micron, Elsevier).

Recent Research Progress and Future Tasks

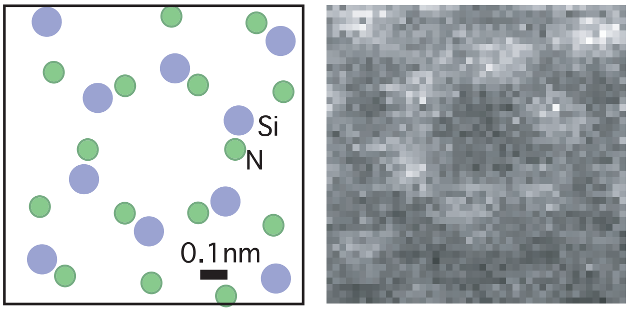
Among various techniques in electron microscopy, STEM and EELS have become the most widely noticed analysis techniques in these years. The reason for this is that there has been a need for more advanced "analysis" results, not just an observation of shapes, for the materials and devices.

After our publication in Nature, similar measurement results are published in a prominent journal (Muller *et al.*, Science **319** (2008) 1073). The fact that element analyses can be done for each atomic position, different from mere average composition analyses, has a large impact on the materials science. It is a step forward toward the ultimate analysis of single-atom discrimination from the conventional understanding of materials through the stoichiometry analyses. Advanced materials require advanced characterizations, in which small amount of additives/dopants that govern the material properties should be analyzed.



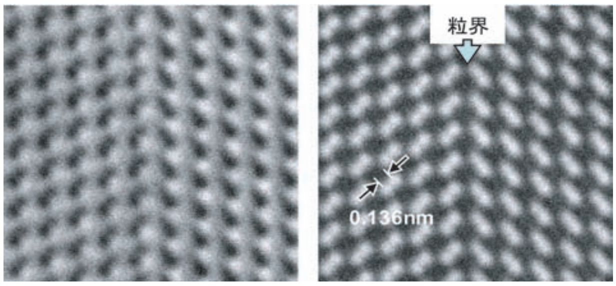
(a) Bright-field image (b) Annular dark-field image

Fig. 3 (a) Bright-field image and (b) Annular dark-field image of β-Si_3N_4 by STEM
Superposed on each image are, expanded view (yellow frame), structural model and simulation image (dotted frame). Detailed structural analyses will be done based on quantitative analyses of the STEM images.



(a) Crystal structure model (b) Distribution image of Si elements

Fig. 4 An example of observation of Si distribution in β-Si_3N_4



(a) Bright-field image (b) Annular dark-field image

Fig. 5 An example of STEM observation of Σ 3 grain boundary in polycrystalline silicon
This method can readily be applied to local regions like grain boundary.

Published Research Papers

1) K. Kimoto, T. Asaka, T. Nagai, M. Saito, Y. Matsui and K. Ishizuka, Nature, **450**(2007) 702.
2) *Nihon Keizai Shimbun, Nikkan Kogyo Shimbun and Nikkei Sangyo Shimbun*, dated Oct.29, 2007.
3) K. Kimoto *et al.*, J. Electron Microsc., **56**(2007) 17.
4) K. Kimoto *et al.*, Appl. Phys. Lett., **83**(2003) 4306, *ibid* **84**(2004) 5374.
5) K. Kimoto, K. Ishizuka and Y. Matsui, Micron, **39**(2008) 257.

2. Electrochromic Display Device

■ The Point of the Research

We have fabricated organic-metallic hybrid polymers consisting of coordination bonds and made clear their structure by using an atomic-force microscope and others. We discovered their excellent electrochromic properties based on electrochemical control of the metal-to-ligand charge-transfer (MLCT) absorption, and succeeded in applying it to solid state devices. A series of results suggest a possibility of applying the hybrid polymers to energy-saving devices such as color electronic paper. A large knock-on effect is expected in all fields of polymer science/technology/industry.

■ Contents of the Research

Electronic paper is drawing attention as one of next generation display devices to follow the liquid crystal, plasma, and organic electro-luminescence (EL) displays. Unlike the present display devices, the display continues after the power is cut. Therefore, it is expected to play the role of paper media for newspapers and others in the future, as a resource and energy saving display device. Up to now various methods are proposed as the display mechanism for electronic paper including the micro capsule method. However, most of them are monochromatic (black and white) display and realizing color display is the task to be achieved.

As a scheme suitable for color display, electrochromic display (a display method using an electrochromic material which changes color through the electrochemical oxidation-reduction process) is known, but only a small amount of research is being pursued compared with other methods. The reason is twofold: one is due to its own proper drawbacks (material's low durability, slow response, difficulty in making solid-state devices), and the other is due to extremely strong dependence on the material's superiority or inferiority of this method's value. To put it the other way around, if the material is developed that is suitable for the application to electronic paper, it is possible that this method could become the breakthrough of color electronic paper.

Aiming at fabricating new materials which possess useful electrochromic properties, we developed organic-metallic hybrid polymers (Fig. 1b). These polymers are formed by self-assembly of metallic ions and organic compounds which have two sites having strong coordination toward metallic ions (organic modules). They develop color through absorption based on charge transfer from metallic ions to the organic modules (MLCT). We discovered the phenomenon of color disappearance on the polymer according to the applied electric potential (electrochromic phenomenon), when we cast this polymer onto ITO glass and electrochemically caused oxidation-reduction. This transition between color development and color disappearance occurs at the threshold voltage corresponding to the oxidation-reduction potential of the metal in the polymer.

So, we fabricated electrochromic display devices using this polymer. By spincoating ITO glass with the polymer and covering it with a layer of gel electrolyte and another sheet of ITO glass, we fabricated the device 5 inches in dimension as shown in Fig.1a.

By applying an electric potential (3V) with two dry batteries, we could repeat alternately development and disappearance of color (Fig.1c).

From now on, researches on electronic paper by using this material are expected to flourish.

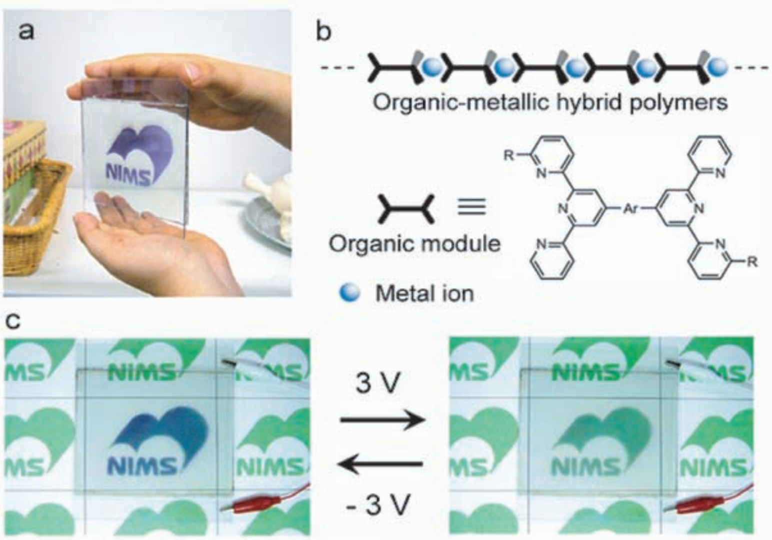


Fig.1 Organic-metallic hybrid polymer having electrochromic property

Key Material for Electronic Paper

Major results

Hybrid polymers can develop various colors with different combinations of organic modules and metallic ions (Fig. 2). We also confirmed their stability by repeating the color development 4,000 times; they have higher stability than usual organic electrochromic materials.

Furthermore, by using these polymers, we succeeded in fabricating display devices 10 inches in size (Fig.3) and devices which can display 5 patterns by changing voltage (Fig.4). We have found that this hybrid polymer can display 3 colors within a single layer film by introducing two kinds of metallic ions into polymer chains and by changing voltage. It is, therefore, expected that researches on electronic paper which can display multi-colors within a thin film as the device will be developed.

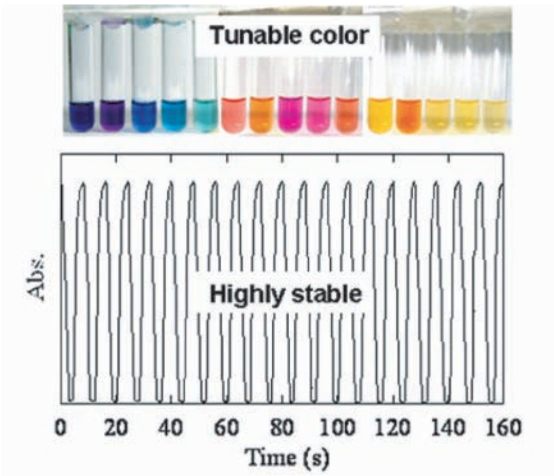


Fig. 2 Multi color display with hybrid polymer

Fig. 3 Display device 10 inches in size using hybrid polymer

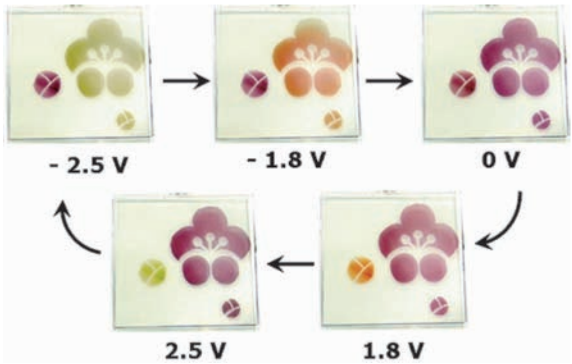


Fig. 4 Multi-color change of display device with voltage

Published Research Papers

1) M. Higuchi and D. G. Kurth: Chemical Records **7**(2007) 203.
2) F. Han, M. Higuchi, and D. G. Kurth: J. Am. Chem. Soc. **130**(2008) 2073.
3) Masayoshi Higuchi: Kagaku Kogyo **58**(2007)33.
4) Domestic Patent 2007-115927

Expected Innovation

This hybrid polymer has solved problems which previous organic electrochromic materials have: stability in repeated operations and control over color tone; and is expected to be a key material for color electronic paper from now on. Furthermore, it will become possible to design and develop larger varieties of hybrid polymers, including this hybrid polymer, by combining various kinds of organic modules and metallic ions. Therefore, in the near future, hybrid polymers will become an important field in polymer chemistry and are expected to influence polymer science /technology/industry.

INQUIRIES

WPI Center for Materials Nanoarchitectonics (MANA) Masayoshi Higuchi

Explanation of the Research Area

Why does Electronic Paper Draw Attention?

Electronic paper is drawing attention as a next generation display device. It is an energy-saving display medium which is light, flexible, and like a real sheet of "paper" retains display even after power off.

To begin with, there are two reasons why the electronic paper draws attention. First, it is because development of "energy saving" display devices is desired. Today, with development of IT represented by Internet, daily life has become more convenient and the life style itself is going to change. However, on the other hand, electricity consumption due to equipment like PC and the amount of discharged carbon dioxide are growing annually, and this dark side of civilization has come to the point where it cannot be ignored. In spite of this, for the present conventional display devices (liquid crystal, plasma or organic EL) irrespective of differences in display scheme, it is necessary to continue to supply electricity in order to keep looking at the image. In contrast, in the case of electronic paper, light reflection is used to see an image just like paper, and since it stores information, it is not necessary to keep supplying electricity to see the image. Electronic paper deserves to be mentioned as an energy-saving display device.

Another reason is, it is expected to contribute to "resource-saving" as it reduces the amount of paper. Before the time of PC, all documents were written on paper. In those days when PC became widespread, many specialists expected that the time of paper-less society would come. Strangely enough, the amount of paper usage which had been expected to decrease due to wide use of PC actually seems to be increasing today. This is because people are printing letters and images on the screen of a PC on paper, which means a liquid crystal monitor device cannot satisfy people's physiological feeling of ease and comfort which printed paper allows. On the other hand, electronic paper can continue displaying like real paper without electricity, is portable and can be stored on a pile. In the future, if it substitutes paper which is now used as a medium for the regularly issued newspapers or journals, it will greatly contribute to the reduction of the resource — paper. For these reasons, the next generation display "electronic paper" is drawing attention both from "energy-saving" and "resource-saving" points of view.

The Display Methods of Electronic Paper

The display methods of electronic paper which are being researched today include electrophoretic method, liquid crystal method, powder displacement method, and chemical reaction method. Within each method, there are several "types" according to corporations and researchers. Representative types are: micro-capsule type (electrophoretic method), cholesteric liquid crystal type (liquid crystal method), electric powder liquid type (powder displacement method), and electrochromic type (chemical reaction method).

Most of electronic paper is basically monochromatic (black and white). Today, however, making it multicolor or full color has become a research objective. In the case of monochromative display, the electrophoretic type with its superior visibility is one up in commercialization. It is commercialized in electronic books (Fig. 1), mobile phone (Fig. 2), and ornamental watches (Fig. 3). In the case of color display, on the other hand, chemical reaction type, especially electrochromic type is drawing attention. The electrochromic type is considered to be a display method with which multicolor and full color are relatively easily realized, since it is driven based on material's electrochemical chromatic change (electrochromic) and various colors can be developed. In spite of that, this method has not been studied so vigorously. The reason is, this method is "extremely dependent on materials" in that superiority of the device is determined only by the property of the used electrochromic material and "usable electrochromic material" has not been fully developed yet.

Fig. 1 Electronic-book

Fig.2 Mobile phone

Fig. 3 Ornamental watch

Electrochromic Material

Chromic material is a general term for the material which reversibly changes color when a stimulus is given from outside. There are many chromic phenomena, and they are named according to different stimuli as, thermochromic (heat causes color change), photochromic (light causes color change), solvatchromic (species of solvent causes color change), vapochromic (vapor causes color change) and electrochromic (electrochemical oxidization-reduction causes color change) etc. are known. So far, many electrochromic materials have been found; as inorganic materials, molybdenum oxide, Prussian blue, phthalocyanine metal complex etc. are well-known; as organic materials, viologen derivative and conductive polymers are mentioned as their representatives. However, there are not many examples of their application by utilizing their electrochromic properties. The reason is, for inorganic materials there is a problem of processing, and for organic materials there is a problem of their poor stability.

Let's take the example of conductive polymer. Dr. Shirakawa et al., won a Nobel Prize in chemistry in 2000 for their discovery of the conductive polymer, that is, π-conjugate organic polymers like poly-acetylene and poly-aniline, when charge is injected through doping, show a high conductivity. Although it is not generally well-known, such a π-conjugate polymer possesses an electrochromic property. The color of conductive polymer is based on its own polymerization structure. The absorption spectrum shifts to a longer wave length when the length of theπ-conjugate chain is large. If this polymer is electrochemically oxidized or reduced, its structure changes (the length of the conjugate chain changes) and color changes. By employing various synthetic organic reactions, various π-conjugate polymers can be synthesized and consequently the lengths of their conjugate chains are various. Therefore, the electrochromic materials can develop various colors. Electrochromic properties of conductive polymers have already been fully studied for 20 years, and their application has been considered. However, most of them could not be practiced. One big reason has been their low stability. As mentioned already, the electrochromic property shows itself when charge (or electrons) is injected to the material causing its change of structure. As a result, even if the original polymer is stable, the polymer structure after oxidization (reduction) is often unstable against light, heat or air, and consequently the material deteriorates when its is repeatedly operated. To serve in practical use the most important thing is, the material has to be stable and reliable. In this respect organic electrochromic materials have had a large drawback.

On the other hand, recently, we developed "organic-metallic hybrid polymer" which is different from conventional organic polymers, and found this polymer has both color development capability and stability, which successfully led to the application to devices, as mentioned earlier.

Hybrid polymers contain many metallic ions. Therefore they are electrically active. For example, in the case of polymer which contains ferric ions, we have made it clear through cyclic voltammetry measurement that it is oxidized at 0.77V from divalent +2 to trivalent +3 (Fig.4). When the ferric ions are divalent +2, absorption occurs in the polymer due to charge transfer from the metal to the organic site. The absorption wavelength is 580 nm. If, on the other hand, one volt of voltage is applied in order to oxidize electrochemically ferric ions in the polymer, the absorption at 580 nm disappears (Fig.5). Thus, the change in color-development/color-disappearance in hybrid polymers occurs through on/off of absorption due to charge transfer and its control is managed by very stable electrochemical oxidization/reduction of the metallic ions.

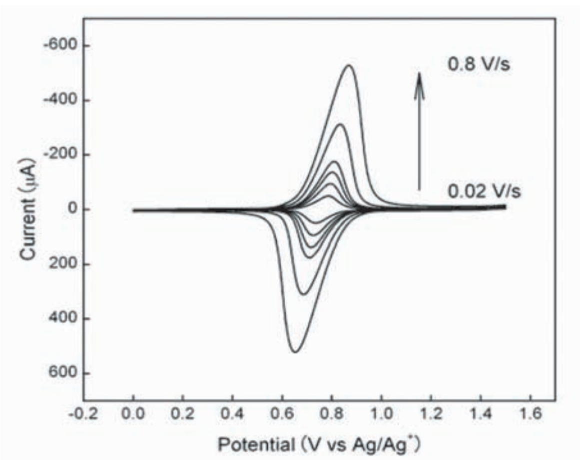


Fig. 4 Cyclic voltammetry measurement

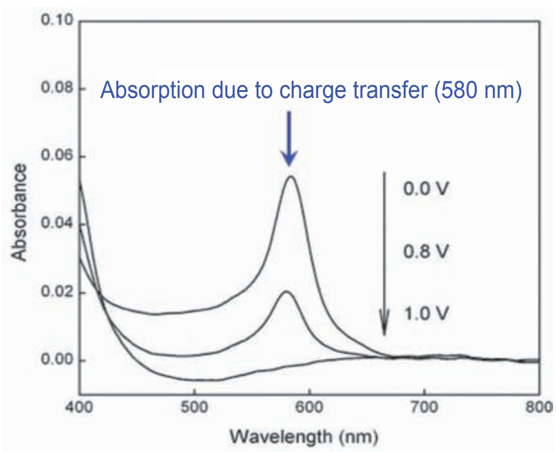


Fig. 5 Change of absorption spectra with voltage application

3. Enhancement of Power Density of Solid-State Lithium-Ion Battery

The Point of the Research

Today Lithium-ion batteries are a key component in advanced information society and used to power portable information equipment including mobile phones and note PC's. They are also highly expected to contribute to the realization of environment-friendly society as the power source for electric vehicles and load leveling apparatus. However, safety issue is intrinsic for the lithium-ion batteries which use flammable organic solvent as electrolyte, which should be overcome to satisfy the global needs. In this research, we have succeeded in enhancing the power density of all-ceramic batteries, which are free from danger of fire or explosion, to be comparable to that of commercial lithium-ion batteries.

Contents of the Research

Background

Lithium-ion batteries are widely used as high-energy density batteries in portable information equipment, such as mobile phones or PC's, and are a key device supporting today's advanced information society. The increasing power consumption in such equipment caused by the increasing throughput year by year requires higher and higher energy density of lithium batteries. On the other hand, efficient use of energy is vital for the realization of environment-friendly society, which will be achieved by popularization of electric vehicles and through load leveling such as storage of night power. Large size lithium-ion batteries are necessary for these purposes and should be developed urgently. However, the lithium-ion batteries which use a flammable material for electrolyte have a crucial problem of safety such as the danger of fire and have difficulty to meet the requirements.

Since a fundamental solution to the problem of safety is to use a noninflammable material for the electrolyte, much attention is drawn to the ceramic, a representative of noninflammable materials, solid electrolyte. The use of solid-state electrolyte, however, considerably lowers the power and makes the performance inadequate for practical use.

Distinctive Feature of the Research

The reason for the small output current from solid-state lithium-ion batteries had been low ionic conductivities of the solid electrolytes. In vigorous researches to solve this problem, several kinds of sulfide solid electrolytes have been developed, lithium-ionic conductivities of which are as high as that of liquid electrolytes. However, even such highly-conductive solid electrolytes had still not improved the power densities of solid-state lithium-ion batteries to be as high as that of batteries sold on the market. In this research aiming at high-power solid-state lithium-ion batteries, we paid attention to the phenomena "nanoionics" at the interface between the electrode and electrolyte in place of exploration of highly-conductive solid electrolytes in the conventional approach.

Because the electrochemical potential for lithium ions in the electrode is quite different from that in electrolyte, when they are in contact to each other, the lithium ions should move across the interface to reach the equilibrium. The movement of the lithium ions promotes the formation of a space-charge layer where the concentration of lithium ions is changed. Furthermore, when the electrode is $LiCoO_2$, the space-charge layer will be highly developed owing to the electronic conduction in the $LiCoO_2$, which should be a highly-resistive layer lowering current drain from the battery.

In this research, in order to suppress development of the space charge layer originating from the difference in electrochemical potential and electronic conduction in $LiCoO_2$, a layer of oxide solid electrolyte was interposed as a buffer layer between $LiCoO_2$ and sulfide solid electrolyte (Fig.1).

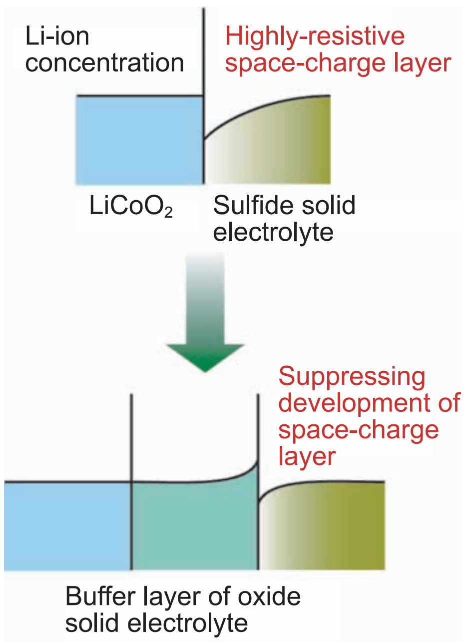


Fig. 1 Schematic drawing of interface between cathode material ($LiCoO_2$) and sulfide solid electrolyte

Lithium–Ion Batteries are Safe

Major results

The electrode in a solid-state battery is a composite of powders of the active material and solid electrolyte to enlarge their contact area. In order to interpose a layer of oxide solid electrolyte between $LiCoO_2$ and solid electrolyte in such an electrode, surfaces of $LiCoO_2$ powders were coated with thin films of oxide solid electrolytes including $Li_4Ti_5O_{12}$ and $LiNbO_3$ (Fig.2) by a rolling fluidized coating method, which is a kind of spray type coating method. .

When buffer layers of $LiNbO_3$ were formed on the surfaces of $LiCoO_2$ powders with a few nano-meters in thickness, the electrode resistance was reduced nearly to 1/100. This electrode gave discharge capacity of over 50%, even when the battery was discharged at a large current corresponding to complete discharge in 10 minutes.

Figure 3 compares the performance between the solid-state battery fabricated with the above-mentioned electrode and commercial lithium-ion batteries with a liquid electrolyte. It is clear that the all-ceramic solid-state lithium-ion battery is comparable to those of commercial lithium-ion batteries both in energy density and power density.

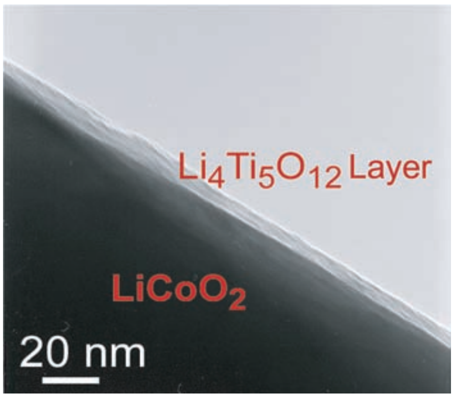


Fig. 2 An example of buffer layer of oxide solid electrolyte formed on the surface of $LiCoO_2$ particle ($Li_4Ti_5O_{12}$)

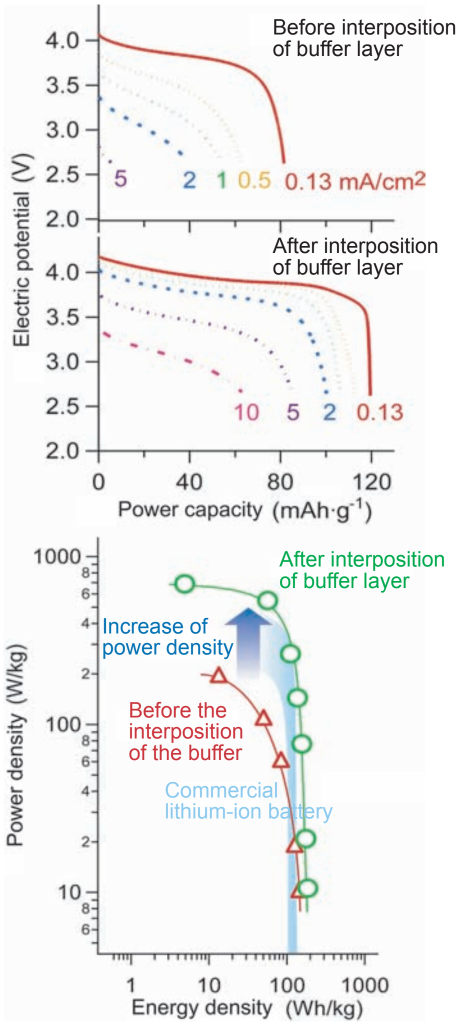


Fig. 3 High-power performance of solid-state lithium-ion battery with electrodes modified by the buffer layers

Published Research Papers

1) N. Ohta, K. Takada, L. Zhang, R. Ma, M. Osada and T. Sasaki: Adv. Mater. **18**(2006) 2226.
2) N. Ohta, K. Takada, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada and T. Sasaki, Electrochem. Commun. **9**(2007) 1486.

Expected Innovation

The results of this research will serve lithium batteries with absolute safety, which break a deadlock to high energy density and large size of batteries to answer the requirements in advanced information society and environment-friendly society. At the same time, they will promote the researches on ion-conduction mechanism at hetero-interface, which are expected to lead to development of new materials based on “nanoionics”.

INQUIRIES

Nanoscale Materials Center Kazunori Takada

Explanation of the Research Area

On the Safety Issues of Lithium-ion Batteries

Electric energy which a battery produces is a product of electric charge stored in the battery and voltage of the battery. The reason for the high energy density of the lithium-ion batteries is their high voltages up to 4 V, which is much higher than 1.2 V ~ 1.5 V generated by other kinds of batteries. Because this voltage much exceeds decomposition potential of water, aqueous solution cannot be used for electrolyte as ordinary batteries. Therefore, organic solvents including ether or ester have to be employed instead. It is the origin of the evil against safety of the lithium-ion batteries, because the organic solvents are flammable.

Because the flammable substances are inside, a lithium-ion battery has to be designed with an enough margin to secure safety. On the other hand, the battery users, such as mobile phones or note PC's, are continuously requiring increasing energy densities for the batteries to respond to the increasing power consumption coming from higher functions of the equipment. Continuous meeting this requirement has made the energy density of the lithium-ion batteries tripled (Fig.2). However, the increase was not brought about by the development of new high-energy electrodes; the cathode and the anode are still $LiCoO_2$ and graphite, respectively. It came from increasing utilization of the electrodes, increasing packing density, and so forth. As a result, the safety margin has become smaller every year in exchange for the increasing energy. Finally, 15 years after their birth, there are many cases of accidents or recall, contrary to the expected security of their safety (Table 1).

In a word, energy densities of lithium-ion batteries have reached a limit as far as the conventional materials are used. The safety issue will be much more severe, when the batteries are installed in electric vehicles, whose broad use is urgently encouraged, because large sized batteries for the electric vehicles contain a large amount of flammable electrolyte, and temperature of the batteries will be readily increased due to poor heat radiation. Safety of such batteries becomes more difficult to secure. For these reasons, realization of safe lithium-ion batteries is more required than ever before.

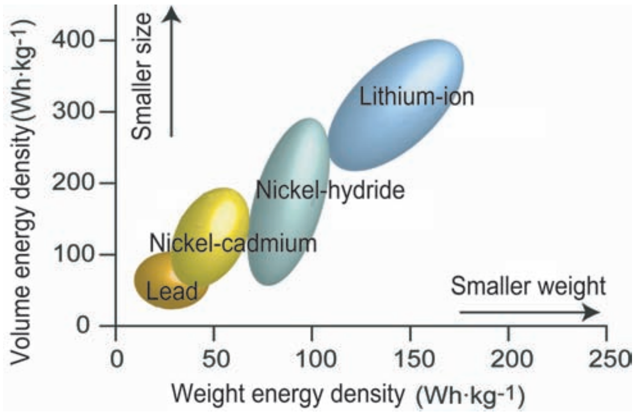


Fig. 1 Energy density of representative secondary batteries

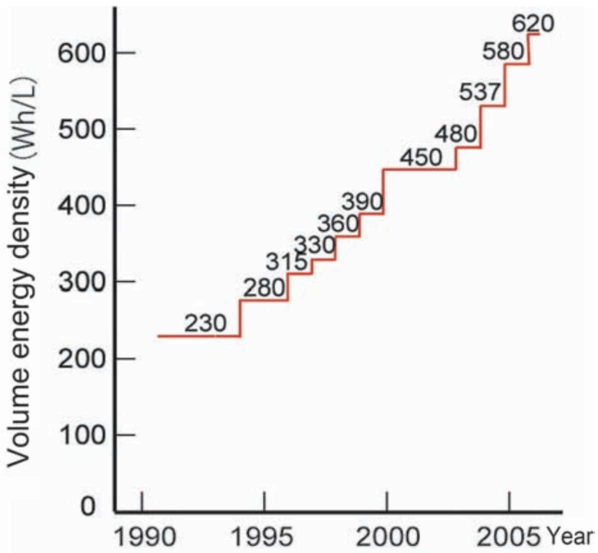


Fig. 2 Trend in energy density of lithium-ion batteries (from data by Matsusita Battery Industrial Co., Ltd)

Table 1 Recent recall for lithium-ion batteries

year	equipment	cause of recall
2006	mobile phone	batteries' swelling
	PC	heat-generation/combustion
	PC	combustion on dropping
	scooter	heat-generation/ combustion
	mobile phone	danger of heat-generation or combustion
2007	mobile phone	batteries' swelling/heat generation
	PC	combustion on dropping
	mobile phone	batteries' swelling/heat generation
	PC	heat-generation/combustion
	mobile phone	heat generation

The Merit of All-Solid-State Batteries

Besides the ceramic material (inorganic material), which has been explained in this article, polymer electrolytes and, sometimes, gel electrolytes are categorized into solid electrolytes; even though the latter contain organic solvent. A notable feature of ceramic solid electolytes different from others, however, is that only particular ions conduct in the ceramic solid electrolytes, the characteristics which other kinds of electrolytes do not have.

In a lithium-ion battery, lithium ions shuttle between the interlayers of $LiCoO_2$ in the cathode and that of graphene in the anode to operate the battery (Fig.3). Therefore, only lithium ions are necessary to be conductive in the electrolyte. However, negative ions and solvent molecules also migrate in a liquid electrolyte. By the way, the reason for the high voltage of lithium batteries is that the cathode and anode materials are strongly oxidative and reducing respectively. Therefore, for example, when solvent molecules diffuse to the surface of the cathode they might be oxidatively decomposed, or reductively decomposed on the anode. Such so-called side reactions taking place in the battery sometimes shorten the operating duration of the equipment or result in self-discharge consuming stored energy even without the operation.

On the other hand, only particular ions are mobile in ceramic solid electrolytes; only lithium ions conduct in that for a lithium-ion battery. Therefore, side reactions described above scarcely occur in solid-state batteries, and thus batteries tend to have a long life and high reliability. Figs. 4 and 5 show performance of solid-state batteries with ceramic solid-state electrolytes. The Li/TiS_2 thin film battery in Fig. 4 has a long cycle life; capacity fading after 20000 charge/discharge cycles is within only 20%. Solid-state batteries with a silver ion-conductive solid electrolyte ($PbAg_4I_5$) in Fig. 5 show very small self-discharge; they retain almost 90% of the capacity after 20 year storage (Fig.5).

Since such performance mentioned above can be expected, and in case of lithium-ion batteries, the safety issue due to organic material electrolyte can be solved, solid-state batteries are regarded as one of the ultimate batteries.

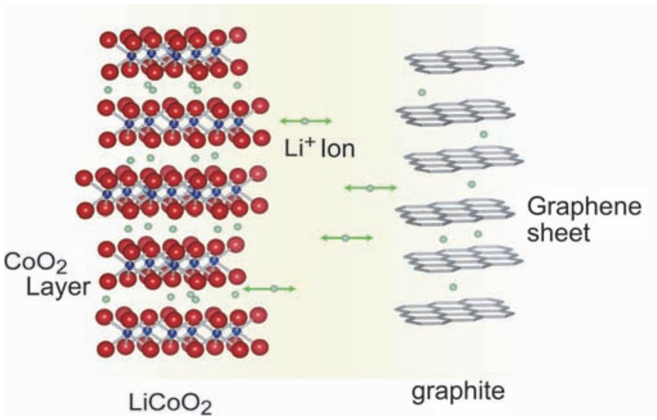


Fig. 3 Operating principle of lithium-ion battery

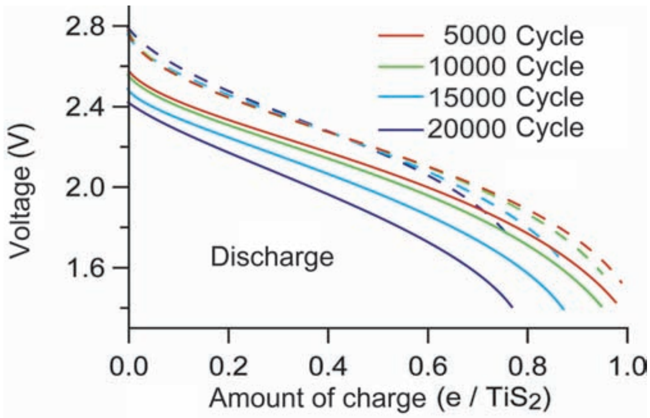


Fig. 4 Charge-discharge cycle characteristics for Li/TiS_2 thin-film battery (Source:S.D. Jones and J. R. Akridge: Solid State Ionics, 86-88(1996)1291.)

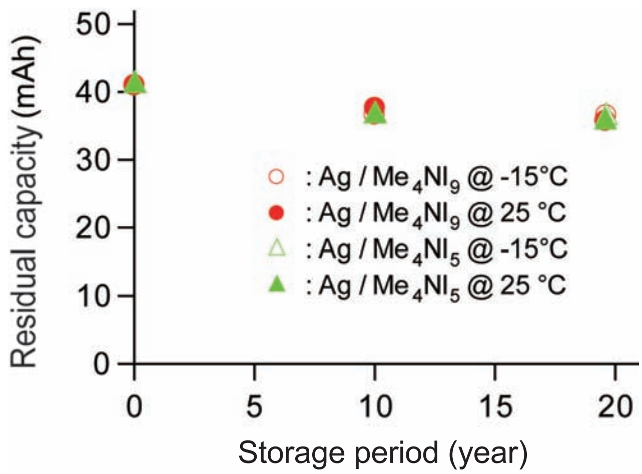


Fig. 5 Storage characteristics of Ag/Me_4NI_9 battery (Source: B.B.Owens and J.R. Bottlelberghe: Solid State Ionics 62(1993) 243.)

4. Research on Quasi Phase-Matching Nonlinear Optics

■ The Point of the Research

1. A device can be realized which converts a laser's fixed wavelength into a desired wavelength with a periodic pattern.
2. In the design of the periodic pattern, the output wavelength can be selected.
3. Various fields of application are proposed such as Laser TV's, ophthalmic treatment, micro processing of semiconductors, high speed optical communication and ultra-high speed electric circuits. A large merit consists in the fact that a suitable design for each application field can be tailored.

■ Contents of the Research

Laser's color (wavelength) is almost fixed by the used material. That is to say, the desired color cannot be obtained from a laser alone; it is necessary to convert the wavelength of the light from a laser in order to change the color. Up to today, a special material has had to be developed for each desired color (wavelength) requiring a long development period.

Quasi phase-matching nonlinear optics is a technique to convert the wavelength freely by forming a striped periodic pattern as shown in Fig. 1. The wavelength can be selected by changing the period. The time will come when a wavelength can be selected freely by patterning.

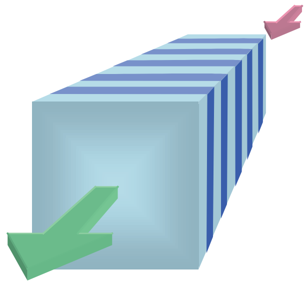


Fig. 1 Quasi-phase matching, nonlinear optical device with periodic pattern

Laser-TV with Green Laser, Ophthalmic Treatment with UV Laser

Some researches are now in progress to realize laser-TV's by using a compact laser device which emits the three primary colors, red, green and blue. However, no semiconductor laser has been successfully fabricated which emits green light. We propose here a quasi-phase-matched wavelength conversion device by using "stoichiometric lithium tantalate $LiTaO_3$", the material developed by NIMS. Fig.2 shows a photo of the wavelength conversion from infrared light to green light with a device made of a periodic pattern fabricated in the material. In the same manner, researches are going on to make vacuum ultraviolet lasers for the purpose of ophthalmic treatment/micro processing by fabricating a periodic pattern in quartz (Fig.3).

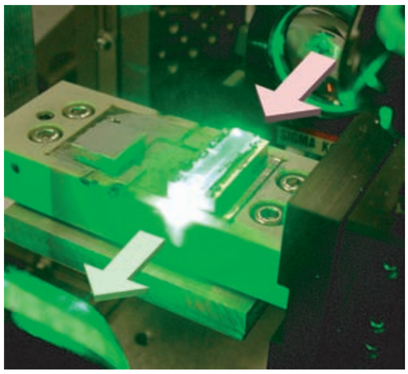


Fig. 2 Compact, high-power green laser with wavelength conversion device

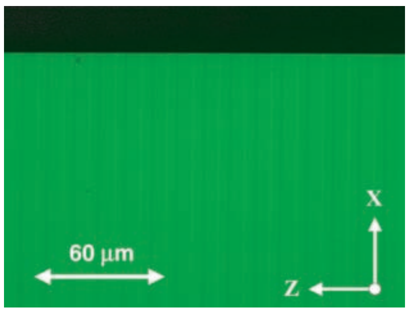


Fig. 3 Fine periodic twin structure formed in quartz (wavelength conversion device to UV 266 nm)

More Capacity for Optical-fiber Communication, Optical Communication in Semiconductor Circuits, too

Owing to the explosive popularization of Internet, capacity of optical communication is rapidly growing. In place of the usual communication method using laser light in a single wavelength, a few tens of different wavelengths are used recently to send information in order to cope with the growth of data capacity. Consequently, wavelength converters are necessary to switch the information among different wavelength channels.

We have realized highly efficient wavelength conversion module for optical fiber communication using quasi phase-matching nonlinear optics (Fig. 4). Technology on high speed optical communication is vigorously pursued also by people in semiconductor manufactures since it can be applied to the data transfer in semiconductor circuits in the future. Fig. 5 shows a cross sectional view of waveguide (a path of light) in a device fabricated on a silicon substrate observed with an electron microscope. It may not be so long before the fast wavelength conversion technique is introduced into silicon semiconductor circuits.

Novel Application of Materials which Wave Conversion Technique Opens Up

■ Major results

(1) We have achieved the world largest output 16W in continuous, single-pass green light conversion. Such performance was realized by fabricating a micro periodic pattern in the magnesium-doped stoichiometric lithium tantalate $LiTaO_3$ which is superior in thermal conduction and light absorption (Fig.2).

(2) We have made it possible to convert the wavelength to UV 266 nm by fabricating a micro periodic twin structure (Fig.3) for the first time in the world on the quartz which is transparent up to vacuum-UV wavelengths and strong against laser damage.

(3) We fabricated a wavelength conversion device for optical communication with a highly confining waveguide and realized the world highest efficiency. We also produced a module (Fig. 4) with the device in the same-principle and succeeded in extracting the timing signals from the ultra-high data signals of 640 Gbit/s. In the same principle, we have achieved the world-top efficiency also in an orthogonal-photon pair generator for quantum optics.

(4) For the first time in the world we have realized dielectric nonlinear optical devices on a silicon substrate (Fig.5). Highly efficient wavelength conversion has become possible in hybrid silicon-photonics. Application to ultra-high speed electronic circuits is expected.

(5) We have demonstrated the world longest device 70 mm in length as a wavelength conversion device in the mid-infrared wavelength region for medical applications (Fig.6) , and achieved the world highest efficiency. Application to small sized lasers for the medical purposes and gas analyses is expected.

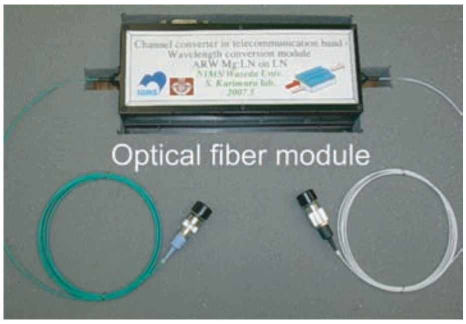


Fig. 4 Wavelength conversion module for optical communication with highly confining waveguide (succeeded in detecting 640 Gbit/s signal)

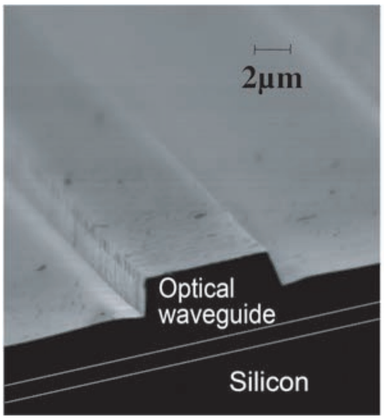


Fig. 5 Wavelength conversion device on silicon substrate


Fig. 6 Long-medium infrared conversion device 70 mm in length (succeeded in wavelength conversion with the lowest threshold value)

Published Research Papers

1) S. V. Tovstonog, S. Kurimura, and K. Kitamura: Appl. Phys. Lett. **90**(2007) 051115.
2) S. Kurimura: Laser Study **36**(2008) 194.
3) S. Kurimura: Kogaku **36**(2007) 232.
4) S. Kurimura, Y. Kato, M. Maruyama, Y. Usui, and H. Nakajima: Appl. Phys. Lett. **89**(2006) 191123.
5) M. Maruyama, H. Nakajima, S. Kurimura, N. E. Yu and K. Kitamura: Appl. Phys. Lett. **89**(2006) 011101.
6) S. Kurimura: *Journal JSLSM* **28**(2008) 404.

Expected Innovation

Through ultimate downsizing of green lasers and UV lasers, a projector on board a mobile phone or laser equipment for in-home ophthalmic treatment can be realized. High output green lasers are also expected to be applied to the field of laser processing. As waveguided devices have high performance capability not only for optical fiber communication but also for optical transmission devices in semiconductor circuits, they have a chance to make a jump to become key devices in computers and mobile phones.

INQUIRIES

Optronic Materials Center Sunao Kurimura
URL: http://www.nims.go.jp/fcg/kurimura

Explanation of the Research Area

In nonlinear optics, it is possible to convert the wavelength of incident light and get output light of different wavelengths. If the phases of output light differ from each other, however, some parts of light become out of phase and diminish. Therefore, in order to make efficiency higher, it is necessary to match the phase. For the sake of phase matching, a periodic structure is fabricated in the nonlinear optical material where polarity of the material is reversed, and the phase is matched at every polarity-reversing block. This technique is called quasi phase matching (Fig.1).

Quasi-phase matching is a technique of realizing nonlinear optical effects (wavelength conversion, etc.) with a high efficiency, by using reversing of spontaneous polarization in ferroelectric substance or reversing of polar axis through twinning in dielectric crystals.

Laser-TV with Green Light Laser

Researches and development are getting vigorous to realize laser TV's or laser projectors with compact lasers which emit the three principal colors, red, green and blue. Although semiconductor lasers are advantageous in power consumption and the life time, no report has been made of successful oscillation in the wavelength region of green, and wavelength conversion is the only way to get green light. We propose here quasi phase-matched wavelength conversion devices by using stoichiometric lithium tantalate $LiTaO_3$ (SLT) which NIMS has developed. SLT has low density of crystal defect, and possesses both high thermal conductivity and low light absorption. Thus the problem of heat, which is a limiting factor of output power, can be mitigated.

These properties become important especially in the green light's high power region. The output 16W, which is higher than the required output 3W for a laser TV, has been achieved by fabricating micro structures for periodic polarization reversal in SLT and by converting infrared light into green one (Fig.2). The output level of green light has reached the power with which a laser theater or laser processing can be aimed for.

Ophthalmic Treatment/Micro Processing with UV Lasers

Lasers in the range of vacuum UV can be applied to ophthalmic treatment and micro processing of semi-conductors. To expand the technique of quasi phase matching to the vacuum UV region, the technology of fabricating periodic patterns onto the quartz which is transparent up to the UV region has been developed. This is a method of fabricating twin structures on a crystal under high temperature and high stress of a few hundred MPa by observing in real time (Fig.3). We are the only group in the world who have this technique. Micro periodic patterns down to 12 micron in period have become possible. Now, as wavelength conversion up to UV 266 nm was achieved (Fig.4), we are advancing researches into the vacuum UV lasers to be applied to ophthalmic treatment/micro processing.

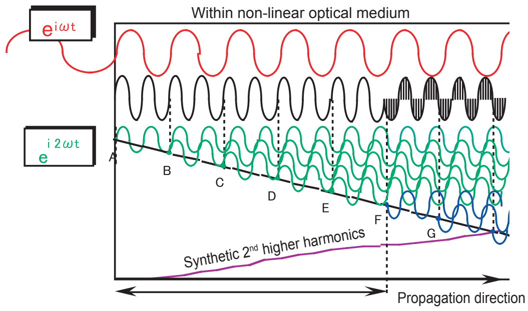


Fig. 1 Principle of quasi-phase matching wavelength conversion Incident infrared light power

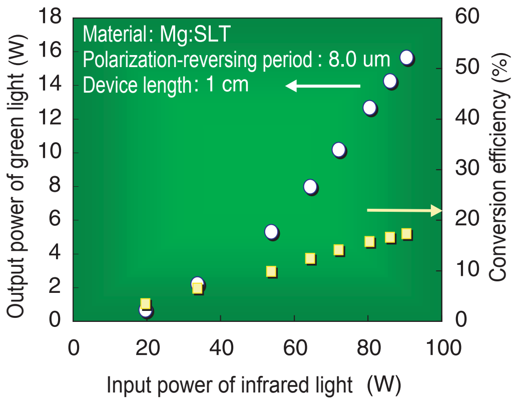


Fig. 2 Wavelength conversion into green light in single-pass, continuous oscillation

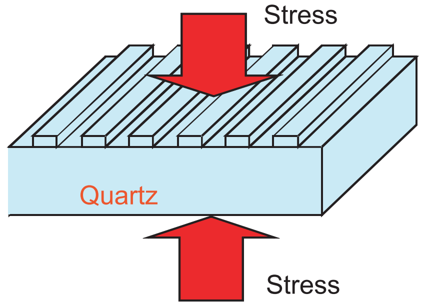


Fig. 3 Formation of periodic twin structure by stress application

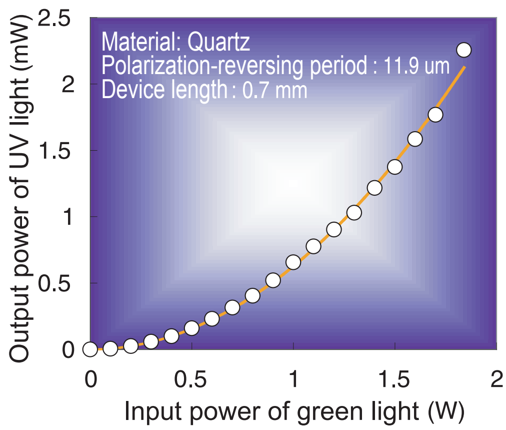


Fig. 4 Wavelength conversion into UV with quartz

More Capacity in Optical Fiber Communication

In a wavelength-division multiplexing system, wavelength conversion plays an important role in order to exchange information among channels with different wavelengths. We fabricated adhered ridge-waveguide devices for quasi phase-matching nonlinear optics and have achieved highly efficient wavelength conversion for optical fiber communication. By making the mode size small in the optical waveguide, the efficiency has become far higher, and we have demonstrated the highest efficiency in the wavelength region of optical communication. Since the small mode-size made it more difficult for a waveguide to couple with optical fibers, we have developed the technique of coupling between an optical waveguide and an optical fiber at the same time, and realized wavelength conversion modules which have small loss.

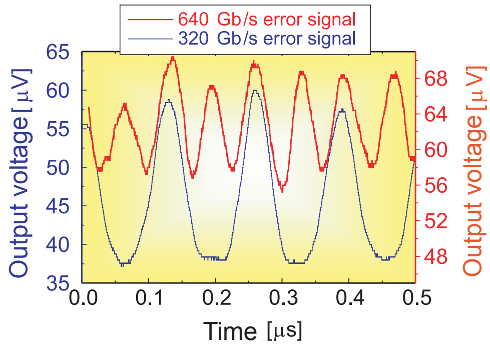


Fig. 5 Comparison of error signals in ultra-high speed transmission experiment

By making the module coupled with fibers, the stability in optical coupling has increased to a large extent making it possible to carry out an experiment on an ultra-high speed optical communication system. Using this module, we have succeeded in extracting timing signals from ultra-high speed data signals of 640 Gbit/s. At this speed of 640 Gbit/s, error signals for feedback can also be obtained in high contrast (Fig.5). This was a system experiment which demonstrated high efficiency and high speed of quasi phase-matching wavelength conversion, indicating that this technique is adequately applicable in ultra-high communication a few generations ahead.

Optical Wiring Also in Semiconductor Circuits

Researches are going on in the area of optical communication on board silicon, so that the technique of optical high speed communication may be applied to the data transfer in semiconductor circuits. Semiconductor manufactures call this technique silicon-photonics and are extensively driving the researches as a technique to replace electric wiring. We realized dielectric nonlinear optical devices on silicon for the first time in the world. Dielectric devices are expected to be key devices in optical wiring in the future, with their merit in high efficiency and high speed.

Mobile Mid-infrared Lasers for In-home Medical Care/Environmental Measurement

Wavelength conversion devices to mid-infrared wavelength regions are anticipated in the field of medicine, for dental treatment and as laser surgical knives, and in the field of environmental measurement like gas-sensing and mass spectroscopy. In general, in case of the wavelength conversion to mid-infrared light, since a high efficiency is difficult to attain, a method of resonating the input light in the resonator is employed to gain efficiency, but the resonator is subject to vibration or temperature changes; stability has been the problem.

We have realized the world-longest device 70mm in length as a wavelength conversion device in the mid-infrared wavelength region, and obtained the world-lowest threshold valve in single-pass wavelength conversion. High-gain device has made it unnecessary to have a resonator, making single-pass operation possible (Fig.6). These high-gain devices are ideal as portable lasers usable for medical treatment or as compact sized laser for environmental measurement, with their low power consumption and small waste heat.

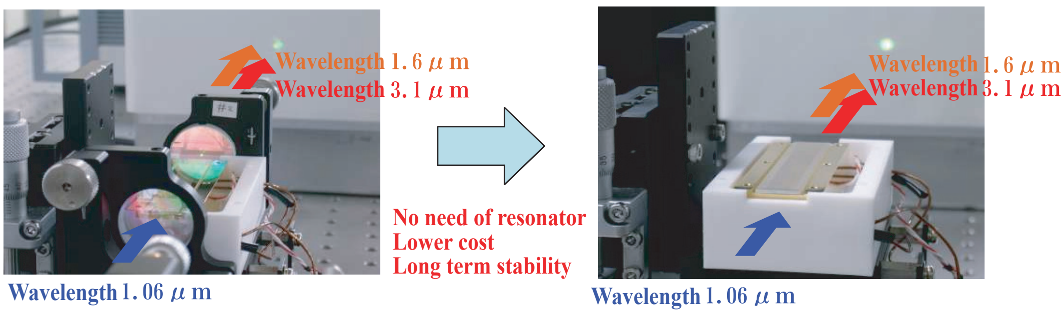


Fig. 6 Wavelength conversion without resonator by 70 mm long converter into mid-infrared wavelength.

5. Development of Tough1500MPa-Class Low-alloy Steel

■ The Point of the Research

We have succeeded in fabricating tough steel with a tensile strength of 1500 MPa by a thermo-mechanical treatment of steel in low-alloy composition which is superior in recyclability and free of alloy elements such as rare metals. The developed low-alloy steel does not break easily on impact, and the impact energy absorption increased more than 5 times compared to that of the conventional 1500 MPa-class low-alloy steel.

■ Contents of the Research

So far, high-strength low-alloy steel has only been able to provide limited application to structural components due to its low toughness especially at a strength level of over 1400 MPa (Fig.1).

We, at NIMS, have paid attention to the fact that the tempered martensite structure is primarily a fine-grain structure consisting of a matrix structure with a hierarchical structure of prior-austenite grain → packet → block →lath and minute carbide particles that are dispersed in the matrix structure as shown in Fig. 2.

We have established a warm-temperature-forming process for tempered martensite (warm tempforming, abbreviated as TF) and succeeded in producing an incredibly tough 1500 MPa-class low-alloy steel by not only fabricating ultra-fine crystal grains of less than 1μm, but also by controlling the shape and orientation of the crystal (Fig.1). By realizing high toughness of the conventional high-strength steel which has had problems relating to safety, we have paved the way for the widening of its application.

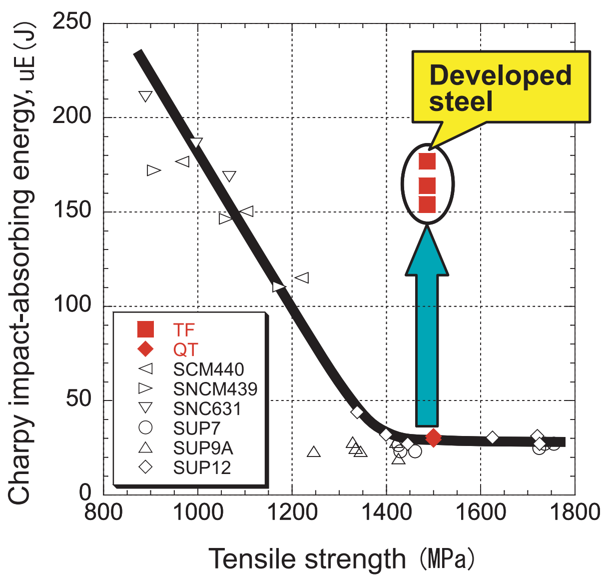


Fig. 1 Relation between tensile strength and Charpy impact-absorbing energy at room temperature for the warm tempformed (TF) steel and the conventional quench-tempered (QT) steel. Data for the JIS steel for machine construction (data 5 (1989) in Data Sheet by the National Research Institute for Metals) and the JIS spring steel (data 9 (1995) in Materials' Strength Data Sheet by the National Research Institute for Metals) are also shown by the open marks.

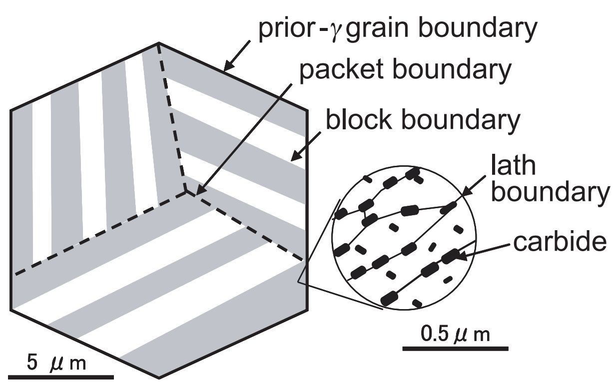


Fig. 2 Schematic drawing of a tempered martensite structure (the conventional quenched and tempered steel). In the tempered martensite structure for medium-carbon steel (C%: 0.3-0.7 in mass %), the average block width of crystal grains which are assumed to be effective for strength and toughness is equal to or finer than a few μm.

High-Strength Steel does not Break in a Snap

■ Major results

(1) We fabricated a rod stock 2cm in cross section and about 1m in length in the deformation processing of a tempered martensite structure of a steel similar to that of a spring-steel alloy with a composition (% in mass) of 0.6%C-2%Si-1%Cr. The processing condition involved a multi-pass grooved roller working applied at 500 degree C with an area reduction of about 80%. We were able to obtain an ultra fine fibrous crystal grain structure with an average minor-axis crystal dimension of 0.4μm and a strong deformation texture with the <110> axis of crystals parallel to the rolling direction (<110>//RD deformation texture) (Fig.3).

(2) In general, when a 1500 MPa-class tempered martensite steel undergoes an impact test, the crack rapidly propagates in the impact direction and splits almost evenly (Fig.4, lower photo). On the other hand, in the developed steel, due to the ultra-fine fibrous crystal grain structures, delamination appears where the crack propagates perpendicularly to the impact direction, similar to breaking a wood stock, and the crack does not propagate easily in the impact direction (Fig. 4, upper photo). As a result, energy absorption increases sharply to 165 J on the average at the strength level of the 1500 MPa-class (Fig.1).

(3) Delamination is considered to result from a large number of {100} cleavage planes oriented parallel to the rolling direction caused by the formation of the <110>//RD deformation texture, in addition to the formation of ultra fine fibrous crystal grain structures.

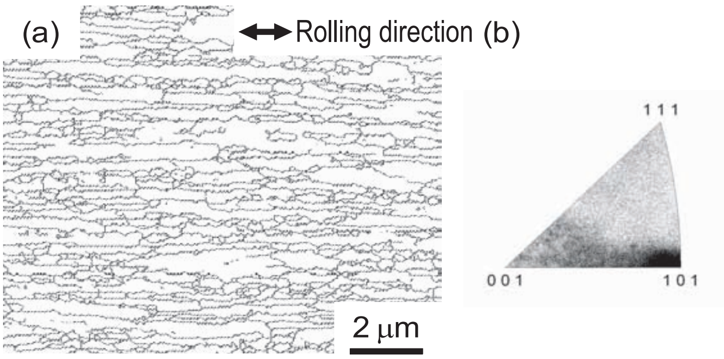


Fig. 3 (a) A map of the grain boundary for crystals whose orientation differs by more than 5 degrees in warm tempformed steel (b) Its inverse pole figure in the rolling direction (RD)

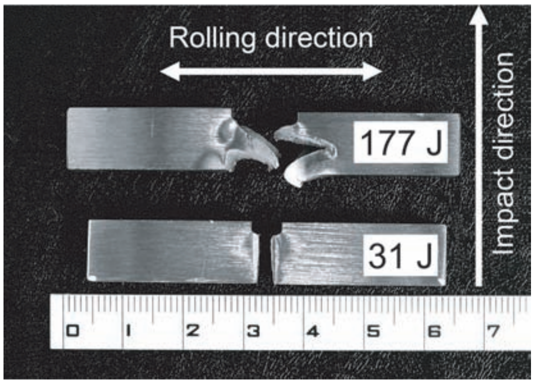


Fig. 4 Photos of the samples after the Charpy impact test. Upper photo: warm tempformed steel. Lower photo: the usual quench-tempered steel. The numbers in the figure show absorbed energy at Charpy impact.

Published Research Papers

1) Y. Kimura, T. Inoue, F. Yin, O. Sitdikov, K. Tsuzaki: *Scripta Materialia* **57**(2007) 465.
2) PCT/JP2006/323248

Expected Innovation

The thermomechanical treatment which we have developed can be applied to a wide range of steels for machine construction including the SCM440 steel, and is expected to become a key technology which realizes ultra-high strength materials for such applications as ultra-high strength bolts/shafts.

INQUIRIES

Structural Metals Center Yuuji Kimura

Explanation of the Research Area

Steel is an important structural material supporting our infrastructure. Recently, the development of high-strength low-alloy steel with a tensile strength in the 1500 MPa-class was highly expected, where its members are superior in recyclability, from the viewpoints of next generation new steel constructions and with the target of reducing the weight of automobiles to suppress CO_2 consumption for global warming prevention. Through the realization of high-strength materials, the amount of the materials is reduced and the design of constructions can also be altered, which is helpful in saving materials and energy; thus it is expected to have a large knock-on effect in reducing the amount of CO_2 emission.

The basic property required of construction materials is the capability to sustain a heavy load. The resistive force against plastic deformation is the yield strength, and the resistance against breakdown is the tensile strength. As the yield stress and tensile strength increase, the amount of load a material can sustain will also increase. When the yield strength of the materials is the same, the material with the smaller density can form lighter members which can sustain the same load. The index for this can be expressed as: the specific strength = yield stress/density. Fig.1 shows the relation between the yield strength and the specific strength for structural metallic materials. If the yield strength of steel is increased to over 1500 MPa, the specific strength becomes 200 kNm/kg which is equivalent to that of extra super duralumin. The density and the Young's modulus are determined only by the chemical composition (alloy composition); however, the yield strength and tensile strength can be increased by controlling the metallic microstructure.

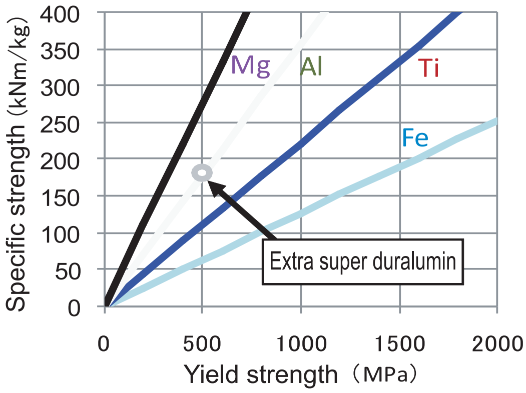


Fig. 1 Relation between yield strength and specific strength

The largest merit for steel materials is that various solid-phase phase transitions between the austenite phase at high temperature and the ferrite phase at low temperature can occur as shown in the Fe-C system phase diagram in Fig.2. By using the solid-phase phase transitions, various metallic microstructures can be formed; a wide range of strength levels can be covered, from 300 MPa to over 5000 MPa (Fig.3)[1]. For example, for martensite steel of low-alloy composition (carbon/alloy steel) strength levels from 600 MPa to over 2000 MPa can only be covered by the quenching of the austenite phase region and by the tempering of the ferrite + cementite phase region. However, properties such as ductility, toughness, fatigue characteristics, hydrogen embrittlement and formability, and higher strength are all engaged in a trade-off relationship. All of these properties determine the applicable strength of high-strength steel.

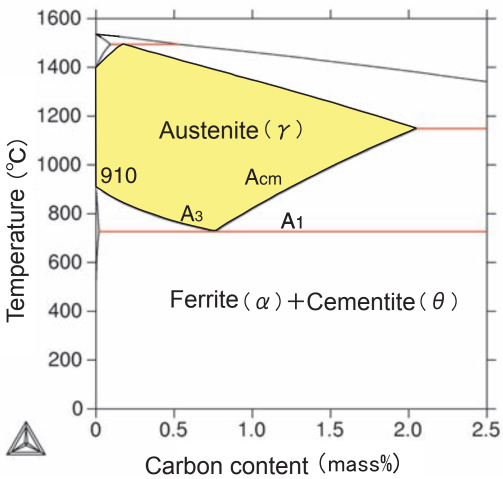


Fig. 2 Fe-C system phase diagram. Since the austenite phase has carbon's solid solubility with a maximum of 2.14 mass %, for steel materials, the volume ratio of cementite which can be used for precipitation strengthening increases to as much as about 30 % at room temperature.

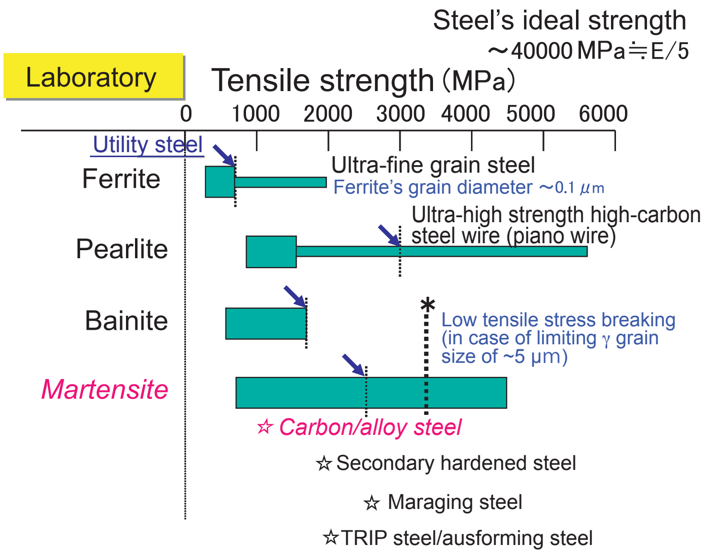


Fig. 3 Relation between the tensile strength and the matrix microstructure in laboratory scale. The blue arrow shows the largest attainable strength[1] for steels in practical use.

NIMS promoted the Ultra-Steel Project (an abbreviation) from 1997 through 2005 aiming at the realization of ultra steel materials with twice the strength and twice the lifetime. As one of the research themes in this Project, we developed a low-alloy steel with a strength of over 1500 MPa which was superior in delayed-fracture resistance and fatigue resistance, and fabricated ultra-strength bolts as a trial[2]. However, even for the 1800 MPa-class steel which had improved its fatigue resistance and delayed-fracture resistance, the impact energy absorption at room temperature was found to be as low as about 30 J. In other words, the toughness was low, and that was the problem.

Usually, high-strength parts such as the 1000 MPa-class high-strength bolts are fabricated by using a softened steel material. The steel is first shaped through cold forging, and then made stronger and tougher through quenching and tempering (Fig.4). However, for ultra-high strength of over 1500 MPa to be realized with the addition of a small amount of alloy elements, the increase of carbon content is unavoidable, making softening difficult. Moreover, when a material is formed into complex shaped parts such as bolts, due to the high content of carbon, not only is formability a problem (Fig.5), but quenching cracks also tended to occur at the bottom of the bolt when the heat treatment was performed[2]. That is to say, for the realization of ultra-high strength parts in the over 1500 MPa-class, not only the properties of the material, but the usual fabrication process also had to be reexamined fundamentally.

The warm tempforming that we developed is a thermo-mechanical treatment method in which the mechanical treatment is carried out after the material is quenched and tempered, with an eye on the formation into the final product. This method does not require the process of softening. Moreover, this method has a merit of improving the materials' toughness drastically by controlling the shape and texture of crystal grains, in addition to reducing the crystal grain size, through the warm deformation of tempered martensite structures.

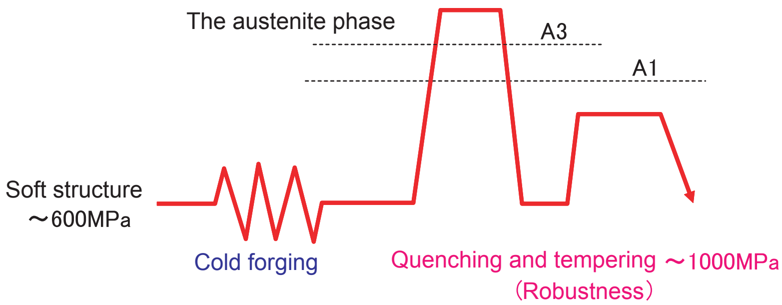


Fig. 4 The conventional thermo-mechanical treatment for bolts. The ordinate is temperature, the abscissa is time. In the mass-production oriented production process of bolts, the head part is usually made in cold pressing and the thread part in cold forging.

Fig. 5 Photo of the formation process of a M22 bolt with the 1800 MPa-class prototype steel developed at NIMS that is superior in delayed fracture tolerance. The head part was formed in hot pressing, since the prototype steel was harder than the usual steel even after the softening process, and it was difficult to form the hexagonal head part in cold pressing. The thread part was formed in cold forging[2].

Published Research Papers

1) Tadashi Maki: The 29-th and 30-th *Shiraishi Memorial Lectures*, The Iron and Steel Institute of Japan (1995)65.

2) Yuuji Kimura, Eiji Akiyama, Kaneaki Tsusaki: Steel Construction Engineering **14**(2007) 121.

6. Metal/Alloy Nano-Particles by Continuous Vacuum Deposition on Surface-Active Running Oil Film

■ The Point of the Research

Metal nano-particles mean metal particles a few nano-meter in dimension, which is the smallest limiting dimension in which solid metals can be formed out of dispersed metal atoms. In terms of the number of atoms, they contain 600 – 5000 atoms. The continuous vacuum deposition on surface-active running oil film is a method to fabricate many kinds of metal/alloy particles on a large industrial scale. It was originally invented by this Institute including the apparatus. This technique is applied in industries to the production of conductive ink, circuit substrates for micro wiring, and pigment ink. Application to other uses is rapidly in progress: sensors, plating solution, catalysts and materials for electrodes of micro-stack capacitors.

■ Contents of the Research

Configuration of Nano-Particles (Fig.1)

Metal particles in nano size are surrounded by ligands and have affinity to the solvent and behave together with solvent molecules. The ligands play the role of a barrier preventing nano-particles from agglomeration. When temperature is raised, ligands are removed from metal particles.

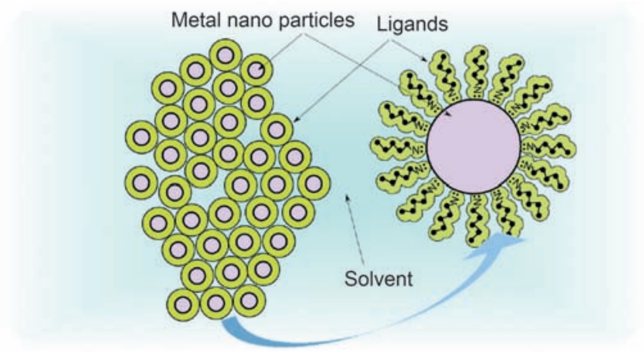


Fig. 1 Form of nano-particles

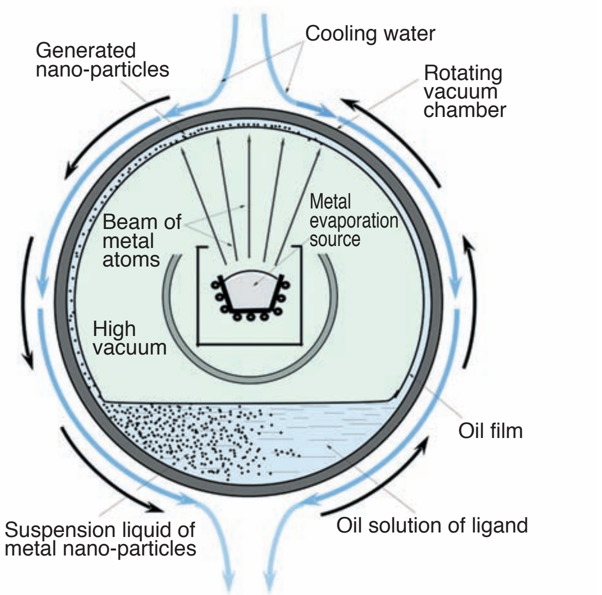


Fig. 2 Principle of generation of nano-particles

Principle of Nano-Particles' Formation (Fig.2)

Nano-particles are formed through vacuum deposition in a rotating vacuum drum. Metal atoms, evaporated and flew from the source, stick on the surface of an oil film containing ligands which spreads out thinly on the inside surface of the drum, and there form nano-particles. The formed nano-particles go downward on the rotating drum and at the same time a new oil film spreads out on the upper part. This process is repeated continuously resulting in a high concentration of the nano-particle dispersion system at the bottom. Particles smaller in size than limiting dimension decompose into metal atoms by evaporating again. On the other hand, particles' growth by combination is suppressed by ligands. Naturally, as a result, the size of particles become uniform.

Macroscopic View of Nano-Particles (Photo 1)

Nano-sized metal particles combined with solvent show a specific color characteristic to the metal species with a beautiful luster, and have lubricious fluidity. As the photo shows, nano-sized silver particles show blue color of metallic luster. When a circuit pattern is printed by using this for ink, and temperature is raised thereafter, a silver circuit wiring is formed. For printing, a high resolution ink-jet printer is used.

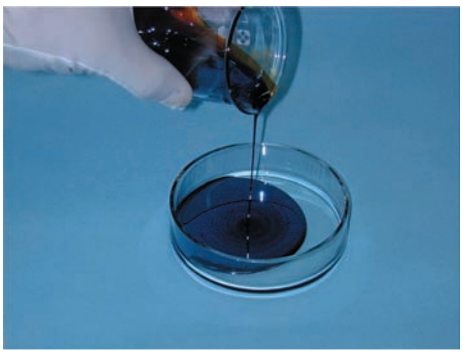


Photo 1. Macroscopic view of nano-particles

Limit in Solid State

■ Major results

Photo 2. Fabrication apparatus type 3 for metal nano-particles. Almost all kinds of metallic nano-particles can be fabricated except for rare-earth metals or high-melting metals.

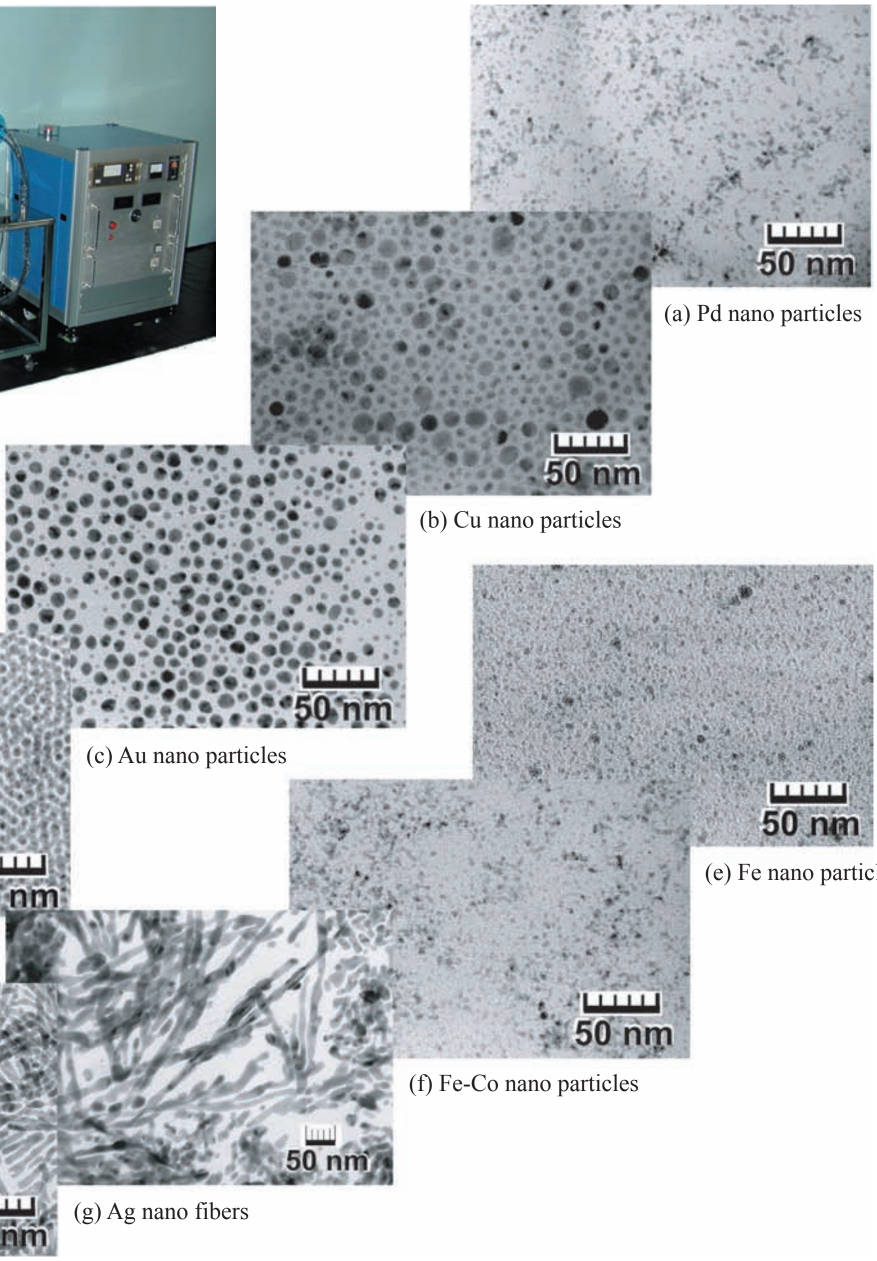


Photo 3. Electron microscope images of various metal nano-particles

Expected Innovation

(1) Glancing at an aspect which concerns the fundamental principle of matters can be done through the researches on nano-particles.

(2) Future use: nano-sized reference materials, catalysts, chip-type batteries, plating solution, anisotropic conductors, etc.

INQUIRIES

Advanced Nano Materials Laboratory Isao Nakatani (Honorary researcher)

Topic 1 NIMS Center for Nanotechnology Network

NanotechJapan	Japan's "Nanotechnology Network" is a Program sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). For five years starting from year 2007, academic, business, and governmental nanotechnology researchers will have the opportunity to use facilities and equipment at 13 network sites with cutting edge nanotechnology. The aim of this Program is to generate research results that will lead to innovations. Fourteen institutions participated in "Nanotechnology Support Project" in the previous term. Now, the number has been greatly increased, and 13 sites and 26 institutions are participating in "Nanotechnology Network", enabling high-level technical support in nanotechnology to various requests from the research community.	NIMS Center for Nanotechnology Network

1. Background and Aim of Establishment

In the US as well as major countries in Europe and Asia, the significance of nanotechnology is now recognized. The nations are setting up nanotechnology research facilities and eagerly promoting their shared use among researchers to make further innovations in the field.

NIMS established "NIMS Center for Nanotechnology Network"(Fig.1) to enhance our capabilities to serve in the Program. It will provide support in the three out of four areas designated by MEXT to cover in the Program - "Nano-characterization", "Nano-fabrication", and "Extreme Conditions".

2. Outline

The center consists of a Coordination Office and three facilities: a Nanotechnology Innovation Center, a High Voltage Electron Microscope Station and a High Magnetic Field Station, all run jointly with Toyo University. “Nanotechnology Innovation Center” (Figs. 2, 3) , on which we put the highest priority, comprises a 2-D nano-pattering foundry, a 3-D nano-integration foundry, a bio-organic materials facility and a silicon foundry run by Toyo University. These four facilities are aimed at creating a comprehensive foundry that will be able to handle an unprecedentedly wide range of materials. At the foundry, research will be conducted on silicon, III-V-based semiconductors, organic/polymeric materials and biomaterials. Magnetic metals will also be added to the range of materials it will study, to develop new substances and high-performance materials.

At “High Voltage Electron Microscopy Common Use Station” (Fig.4), various analytical electron microscopes such as a 1000kV microscope are available for sharing by outside users. “High Magnetic Field Common Use Station” (Fig. 5) offers state-of-the-art 930MHz NMR spectrometer and other common-use instruments. These will be used mainly for measurement, observation and evaluation. NIMS provides its state-of-the-art equipment, including its Beam Line Station at SPring-8, to other organizations to support their research as well.

NIMS Center for Nanotechnology Network also seeks to promote the establishment of information networks, both domestic and international. For that purpose, it has set up the Coordination Office, which coordinates activities of the 13 centers and promotes the establishment of domestic/international networks in collaboration with the Scientific Information Office and the International Affairs Office.

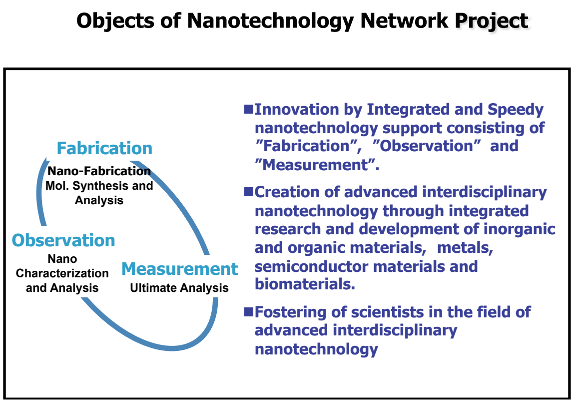


Fig. 1 Objects of “NIMS Nanotechnology Support Network”

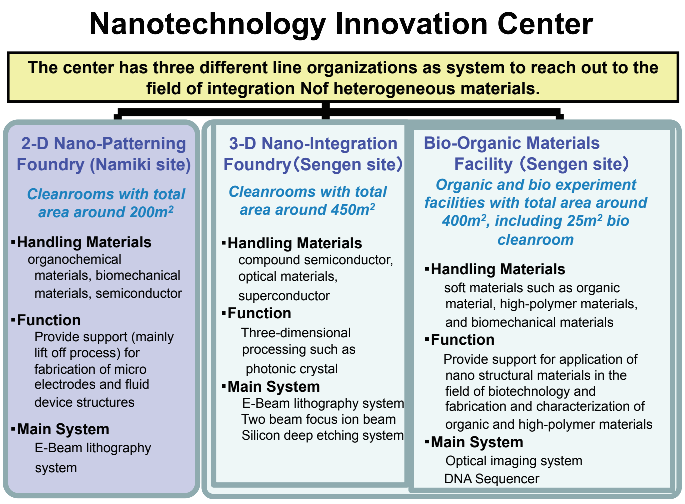


Fig. 2 Outline of “Nanotechnology Innovation Center”

3. Major Activities

(1) Support for "Nano-fabrication" at Nanotechnology Innovation Center

Support has been provided for nano-fabrication with equipment for electron-beam lithography, dry-etching and others, sample preparation and evaluation of and with organic/polymeric materials and bio-materials. In this respect, we have extended support to 116 users including "Development of cell culture platform, with the chitosan-nano-scale fibers which will be on the market starting this year".

(2) Support for "Nano-characterization" at High Voltage Electron Microscopy Common Use Station

Support has been provided for 55 users by characteristic three groups: "Dual-ion beam interfaced high-voltage electron microscope", "High-resolution high-voltage electron microscope" and "Atom-discriminating electron microscope".

(3) Support for Measurements in "Extreme Conditions" at High Magnetic Field Common Use Station

Support has been provided for 94 users including 20 users for 930MHz–NMR which was high in rate of utilization.

(4) Coordination of Nanotechnology Network at Coordination Office

As part of this networking activity, We holds the 6th Nanotechnology Symposium(Tokyo, Feb. 2008), and bilateral workshops between Japan and the US, Europe and other Asian countries and facilitate international human exchanges. And nanotechnology portal site "Nanotech Japan" (http://nanotechjapan.jp/) was created to help advance nanotechnology R&D and catalyze innovation for a target readership of researchers, research managers, and students interested in the area of nanotechnology. The bilingual website (Japanese/English) provides select nanotechnology information and serves as an information gateway to the 13 centers (26 organizations) of the Nanotechnology Network.

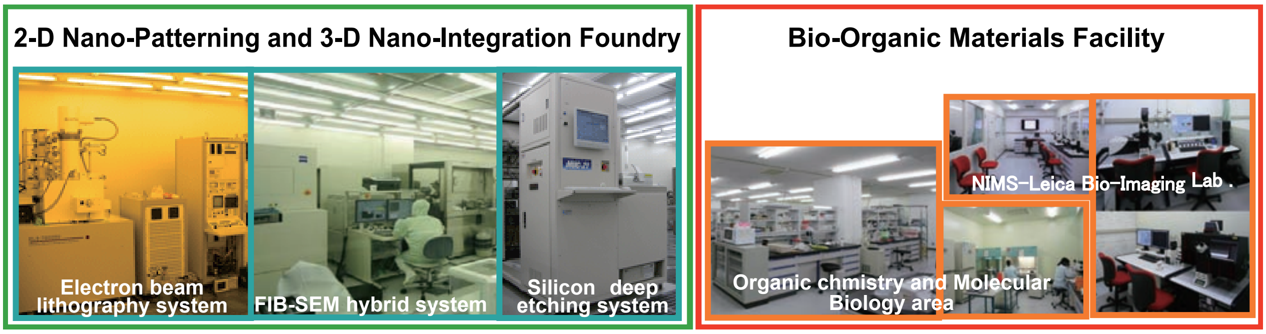


Fig. 3 Major Facilities of "Nano Technology Innovation Center"

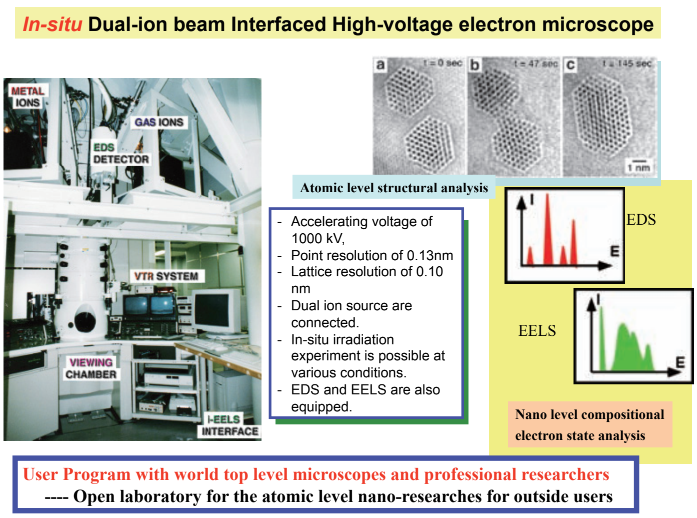


Fig. 4 Major Facilities of "High Voltage Electron Microscopy Common Use Station"

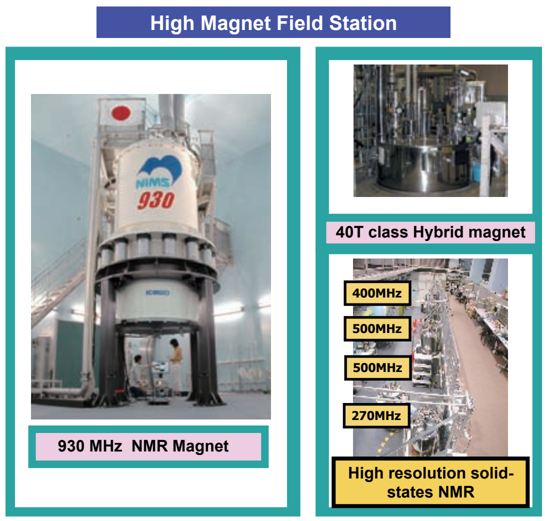


Fig. 5 Major Facilities of "High Magnetic Field Common Use Station"

INQUIRIES	NIMS Center for Nanotechnology Networ Keijiroh Hirahara URL: http://www.nims.go.jp/nsnet

Topic 2 NIMS launches the WPI Research Center, MANA

NIMS has been selected as one of the institutes eligible to receive research grants under the "World Premier International Research Center (WPI) Initiative" in September 2007, sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). The aim of the program is to create research centers with "global visibility" in Japan which can boast extremely high research standards and a research environment that will attract many of the world's top researchers. Following a review of documents and interviews on a total of 33 proposals, NIMS was selected as the only Independent Administrative Institution (IAI), together with the University of Tokyo, Kyoto University, Tohoku University and Osaka University.

MANA

In October 2007, NIMS launched the International Center for Materials Nanoarchitectonics, abbreviated as MANA, as a WPI Research Center.

Four rings of the MANA's logo represent the four key technologies in Materials Nanoarchitectonics. The design as a whole also resembles the structure of an atom, expressing the goal of creating diverse substances and materials with MANA as a nucleus.

What is Materials Nanoarchitectonics?

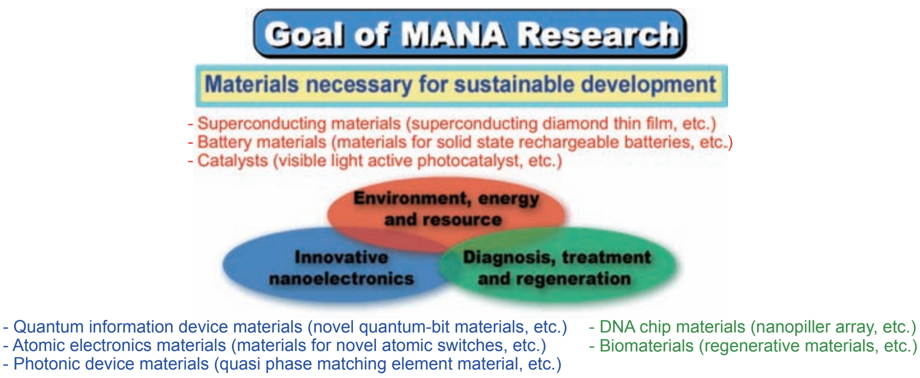
The ultimate research goal of MANA is to develop novel materials that support "sustainable development". As specific targets, MANA focuses on battery materials, superconducting materials, catalysts, quantum devices, atomic devices, optical devices, medical diagnosis materials and biomaterials. In a word, MANA will contribute to solving various serious problems confronting humankind in the 21st century concerning environment, energy, resources, information-communication, medical care and others, from the direction of materials, which is one of Japan's greatest strengths.

As a key feature of MANA, the new center places the new materials development concept of materials nanoarchitectonics[1)] at the center of its research as it strives to achieve this objective. Materials nanoarchitectonics is not limited to creating single nanostructures and elucidating their functions. It is an innovative research concept that aims to extract and utilize the ultimate functions of materials by understanding the mutual interactions of individual nanostructures and intentionally controlling the arrangement of those nanostructures.

Organization of MANA

For realization of the concept of MANA, more than 20 of the world's most outstanding researchers are invited to MANA as Principal Investigators. These researchers come from NIMS and six other institutes, such as the University of Cambridge, UCLA (University of California, Los Angeles), CNRS (Centre National de la Recherche Scientifique, France), Georgia Institute of Technology, University of Tsukuba and Tokyo University of Science.

In addition, approximately 40 young scientists from NIMS, about 40 post-doctoral researchers and 30 graduate students from around the world are selected. A total of 170 staff are working in the project, including engineers and administrative personnel. Among these members, the number of those from foreign countries is 60 (35%), which



1) The term "Nanoarchitectonics" was first used by Aono et al. at the International Symposium on Nanoarchitectonics Using Suprainteractions, held in 2000 in Tsukuba.

already exceeds the program’s aimed value: over 30% of foreign researchers.

NIMS will provide MANA with a whole building in order to centralize researchers and promote integration of different research fields. Furthermore, the six institutions as MANA satellites create a powerful alignment for promoting research and human resources development within the MANA framework.

High Evaluation of NIMS’s Achievements

The reason for the selection of NIMS as the only IAI in the new program in spite of intense competition was the high overall evaluation of NIMS itself as the host institute, as well as MANA's unique research concept of materials nanoarchitectonics. The followings were considered as remarkable achievements to ensure NIMS’s support for realizing the MANA concept.

(1) Excellent research results in nanotechnology and nanomaterials.

(2) World's top-class large-scale research infrastructure, including high magnetic field facilities, ultra-high resolution/ultra-high voltage electron microscopes, NIMS dedicated beamline at SPring-8, etc.

(3) Program for developing outstanding human resources for research, centering on the International Center for Young Scientists (ICYS).

(4) Wide variety of international collaboration projects, including the World Materials Research Institute Forum and the International Joint Graduate School Program, etc.

Continuing System Reform

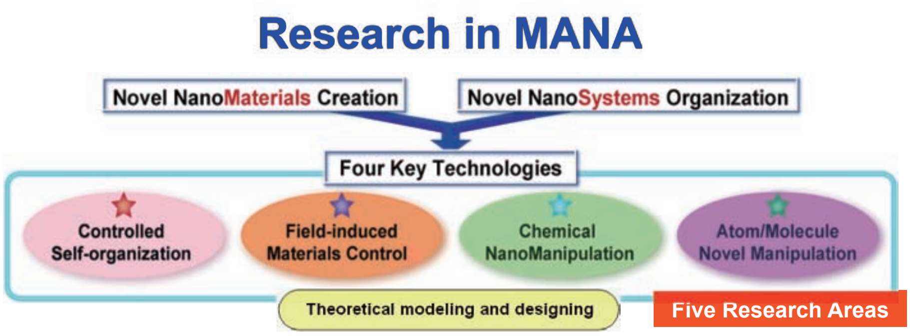
In spite of its impressive achievements to date, NIMS is not resting on its laurels. We intend to develop research at the world's highest level in the MANA project. In order to realize this, a world-class research system is also necessary. Therefore, simultaneously with advanced research in MANA, NIMS will also continue its innovative efforts to realize systemic reform, including ongoing internationalization, the introduction of a tenure track system for researchers, development of human resources, and reforms in the administrative division.

In 2003, NIMS launched a project called the International Center for Young Scientists (ICYS) with financial support from MEXT's Special Coordination Funds for Promoting Science and Technology, and worked for five years on fostering young researchers and creating an environment in which international researchers could work easily. In MANA, we will further strengthen these efforts so that NIMS can evolve into an international core research institute.

Goals of MANA

This program will continue for at least 10 years, and will be extended for an additional 5 years for centers with particularly high achievements. The goal of the MANA concept is not only to develop MANA into one of the world's core institutes in nanotechnology and nanomaterials research 10 years from now, but also to ensure that NIMS itself evolves into the world's top materials research institute, with MANA in the leadership role.

"Mana" is a word of Polynesian/Melanesian origin that means a supernatural power to bring about good fortune or magical powers. Likewise, the MANA concept will play a key role in achieving our ambitious goals. With this new initiative, we expect dramatic progress at NIMS in the next 10 years.



INQUIRIES	International Center for Materials Nanoarchitectonics (MANA) Takahiro Fujita URL: http://www.nims.go.jp/mana/

Statistics Concerning NIMS Operation in FY2007

- Number of citations
- Trend in number of papers
- Trend in number of patents
- Finance and personnel
- External funds
- Grant-in-aid scientific research
- Organization of NIMS Center for Nanotechnology Network
- NIMS Organization

Number of citations

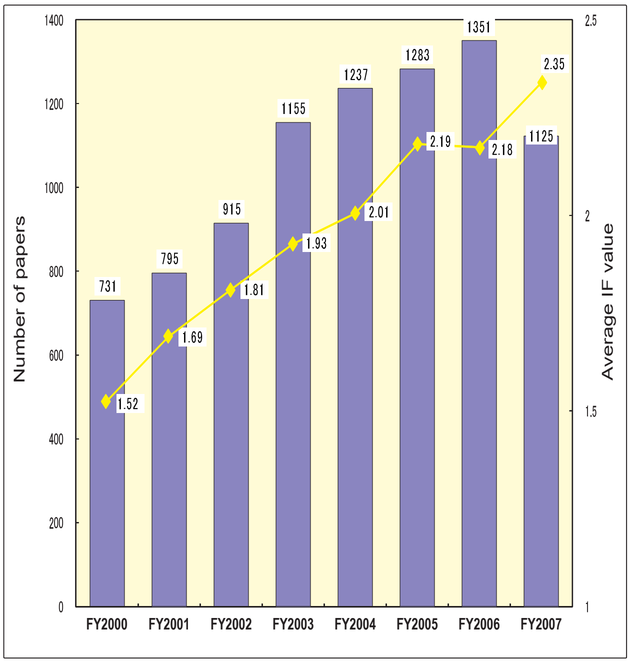
Citation ranking (in Materials Science)

Before NIMS establishment (1996-2000)			After NIMS establishment (2004-2008)		
1	Max-Planck Institute	4,886	1	Chinese Academy of Sciences	24,612
2	Tohoku University	3,990	2	Max-Planck Institute	12,761
3	University of California, Santa Barbara	3,204	3	Tohoku University	9,538
4	MIT	3,095	4	NIMS	8,481
5	Russian Academy of Sciences	3,026	5	AIST	7,589
6	University of Cambridge	2,570	6	National University of Singapore	7,568
7	AIST	2,561	7	MIT	7,503
8	Pennsylvania State University	2,517	8	Tsinghua University	7,110
9	Kyoto University	2,443	9	Seoul National University	6,364
10	Osaka University	2,370	10	University of Cambridge	6,318
:		:			
31	National Research Institute for Metals and National Institute for Research in Inorganic Materials	1,570			

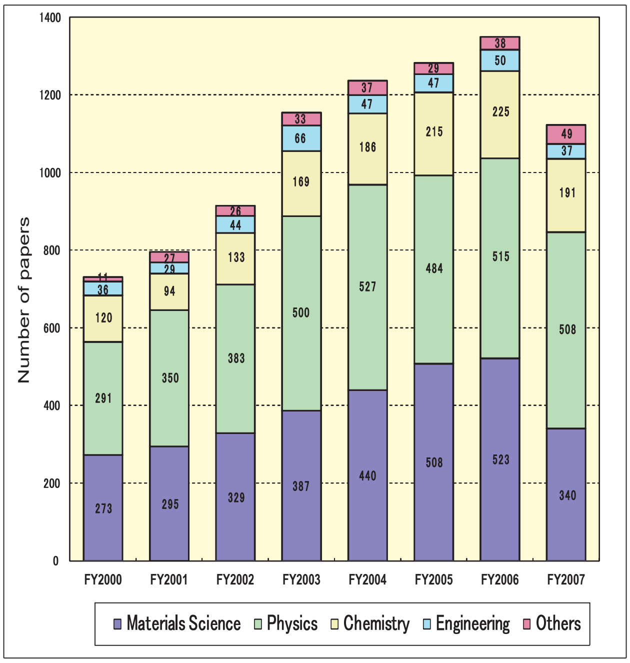
● This ranking was made based on ESI database of Thomson Scientific as of Sep. 2008.

Trend in number of papers

Number of SCI papers and average impact factor



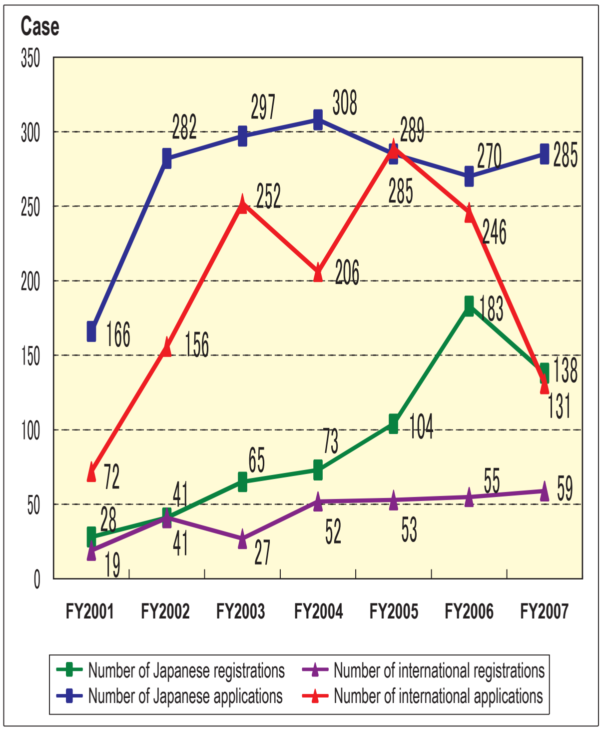
Paper Classification by Field



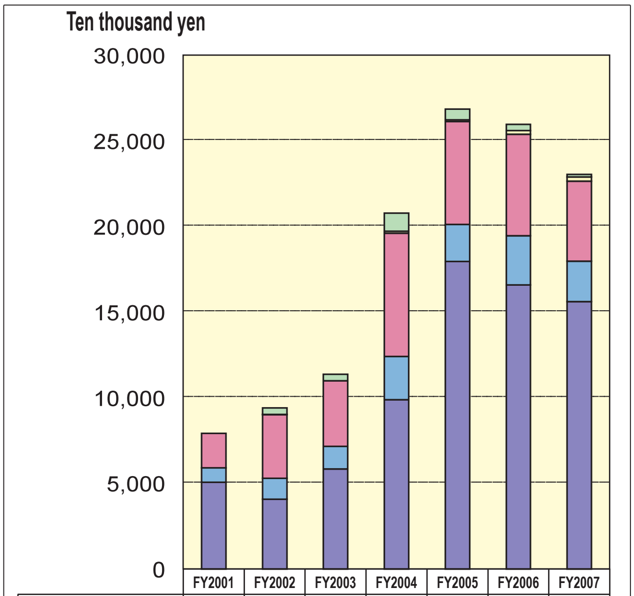
● Analysis based on the Web of Science database provided by Thomson Scientific.

Trend in number of patents

Number of applications and number of registrations



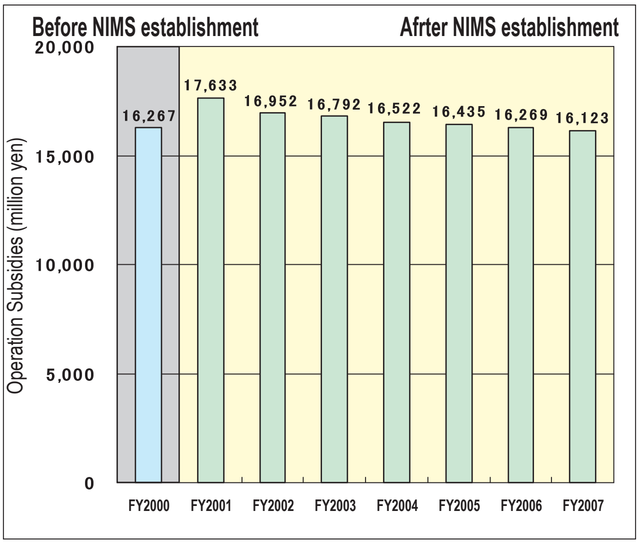
Patent-related expenses



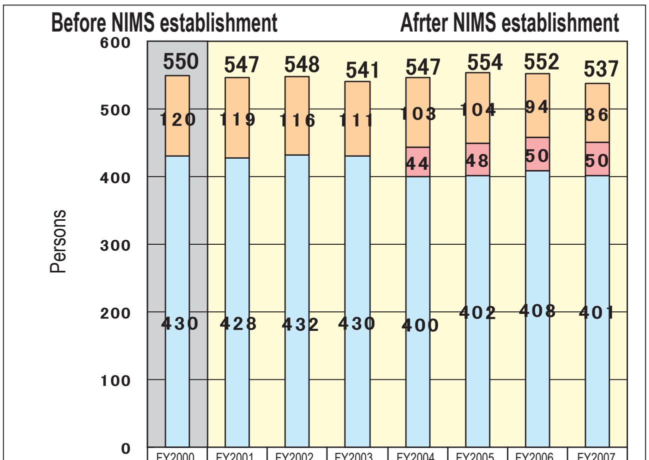
	FY2001	FY2002	FY2003	FY2004	FY2005	FY2006	FY2007
Patent-related miscellaneous expenses	0	366	386	1,054	624	352	141
Japanese: registration/ maintenance fee	0	5	0	111	111	229	249
Japanese: application/ examination certificate fee	2,021	3,729	3,824	7,204	6,004	5,912	4,680
International: registration/ maintenance fee	839	1,231	1,324	2,521	2,153	2,879	2,351
International: application/ examination certificate fee	5,066	4,073	5,839	9,890	17,963	16,587	15,616

Finance and personnel

Trend in Operation Subsidies



Trend in number of permanent staff



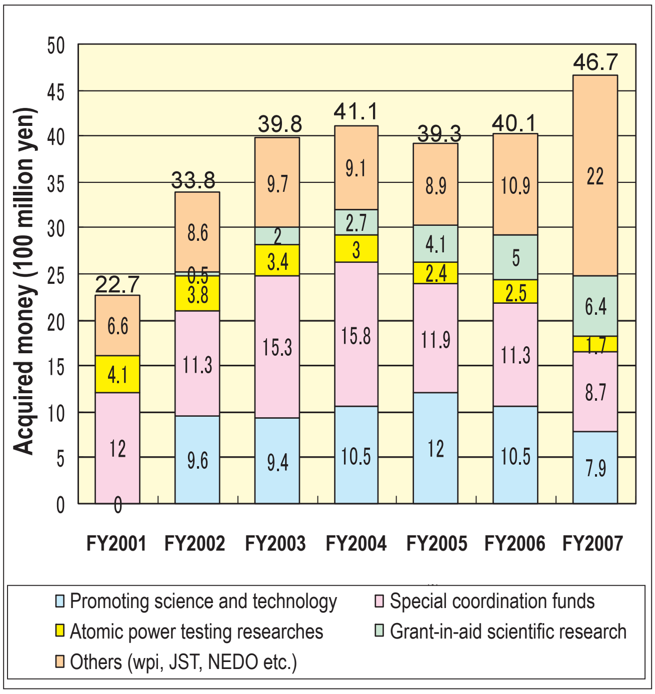
	FY2000	FY2001	FY2002	FY2003	FY2004	FY2005	FY2006	FY2007
Administrative staff	120	119	116	111	103	104	94	86
Engineers	0	0	0	0	44	48	50	50
Researchers	430	428	432	430	400	402	408	401

●The operation subsiy in FY2000 is the sum of general account (Cabinet Office) allocated for former National Research Institute for Metals and former National Institute for Research in Inorganic Materials. After FY2001, it is the sum of operating subsidy and subsidy for facilities.

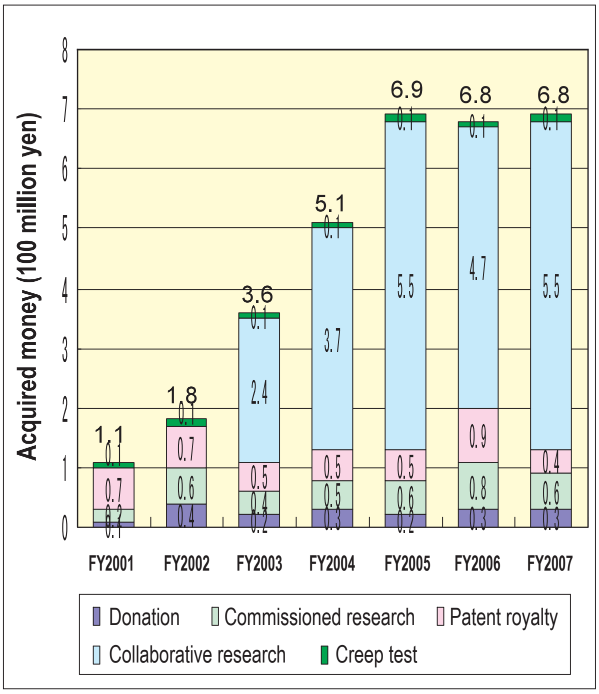
●Number of personnel at each fiscal year end (board members are excluded).

External funds

Competitive funds

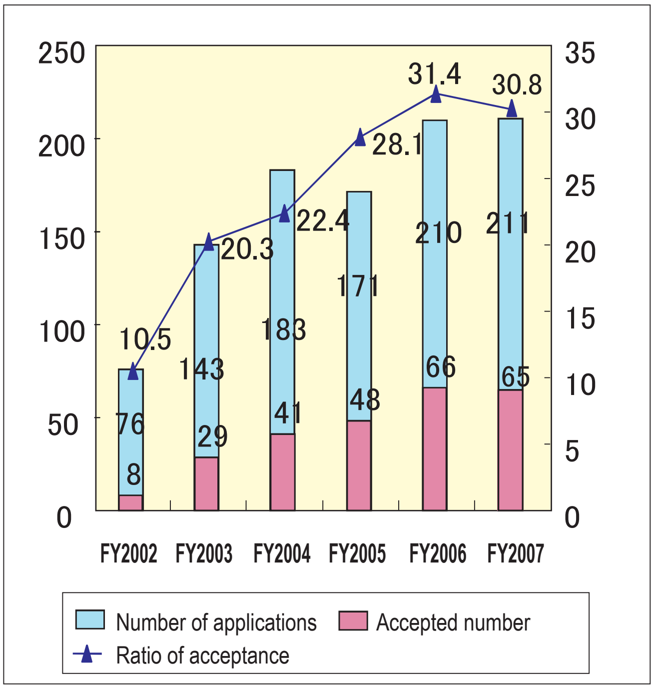


Funds from enterprises, etc

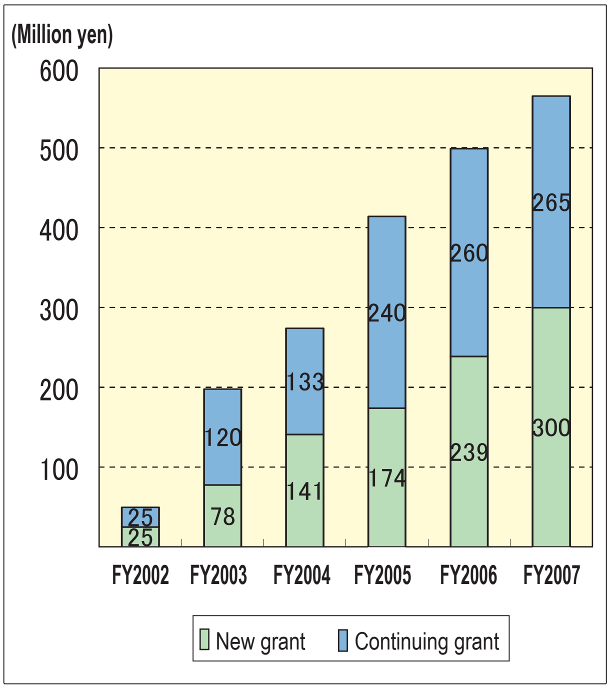


Grant-in-aid scientific research (*Kakenhi*)

Applications and Ratio of acceptance



Amount in money of acquirement



Organization of NIMS Center for Nanotechnology Network

- Director-General
  - Deputy Director-General
  - Steering Committee
  - Coordination Director

Nano Foundries

- Nano-Fabrication of various materials in Nano Foundry Nanotechnologr Innovation Center
  - 2-D Nano-Patterning Foundry
  - 3-D Nano-Integration Foundry
  - Bio-Organic Materials Facility
- Toyo University Nanotechnology Network

Ultimate Analysis Facilities

- Advanced Characterization by Ultra High Magnetic Field and Solid State NMR High Magnetic Field Station
  - NMR Facilities

Nano-characterization Facilities

- Nano-Characterization with In-situ, High-resolution and Analytical Electron Microscopy
  High Voltage Electron Microscope Station
  - Dual-ion beam Interfaced High-voltage electron microscope
  - High- resolution high-voltage electron microscope
  - Atom-discriminating electron microscope
- Center for Synchrotron Radiation Nanoscience NIMS Beamline Station at Spring-8
  Joint operation with JAEA and Ritsumeikan Univ.

NIMS Organization

- President
  - Auditors
  - Advisory Board
  - Vice Presidents
  - Assistants/Deputy Assistants to the President
  - Fellows
  - Coordinating Directors

Administration Offices
- Secretary's Office
- Audit Office
- Safety Control Office
- General Affairs Division
- Planning Division
  - President's Office
  - Planning and Coordination Office
  - Research Evaluation Office
  - International Affairs Office
  - Public Relations Office
  - Human Resources Development Office
  - Collaboration-promotion Office
  - Scientific Information Office
  - Information Technology Office

Key Nanotechnologies
- Nano System Functionality Center
- Advanced Nano Characterization Center
- Computational Materials Science Center
- Quantum Dot Research Center
- Quantum Beam Center

Nanoscale Materials
- Nanoscale Materials Center
- Organic Nanomaterials Center
- Nano Ceramics Center

Materials for Information Technology
- Advanced Electronics Materials Center
- Optronics Materials Center
- Magnetic Materials Center

Materials for Biotechnology
- Biomaterials Center

Materials for Environment and Energy
- High Temperature Materials Center
- Fuel Cell Materials Center
- Superconducting Materials Center
- Photocatalytic Materials Center
- Structural Metals Center

Materials for Reliability and Safety
- Material Reliability Center
- Composites and Coating Center
- Sensor Materials Center

Exploratory Research Laboratories
- Advanced Nano Materials Laboratory
- Innovative Materials Engineering Laboratory

Department of Materials Infrastructure
- High Voltage Electron Microscopy Station
- High Magnetic Field Station
- Beam Line Station
- Materials Data Sheet Station
- Materials Database Station
- Materials Manufacturing and Engineering Station
- Materials Analysis Station

Interdisciplinary Cluster

Cluster for New Project

Doctoral Program in Materials Science and Engineering

The Rolls-Royce Centre for Excellence for Aerospace Materials

NIMS Nanotechnology Support Network

International Center for Materials Nanoarchitectonics (MANA)
- ICYS-MANA

ICYS-IMAT

Issuer: National Institute for Materials Science
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