

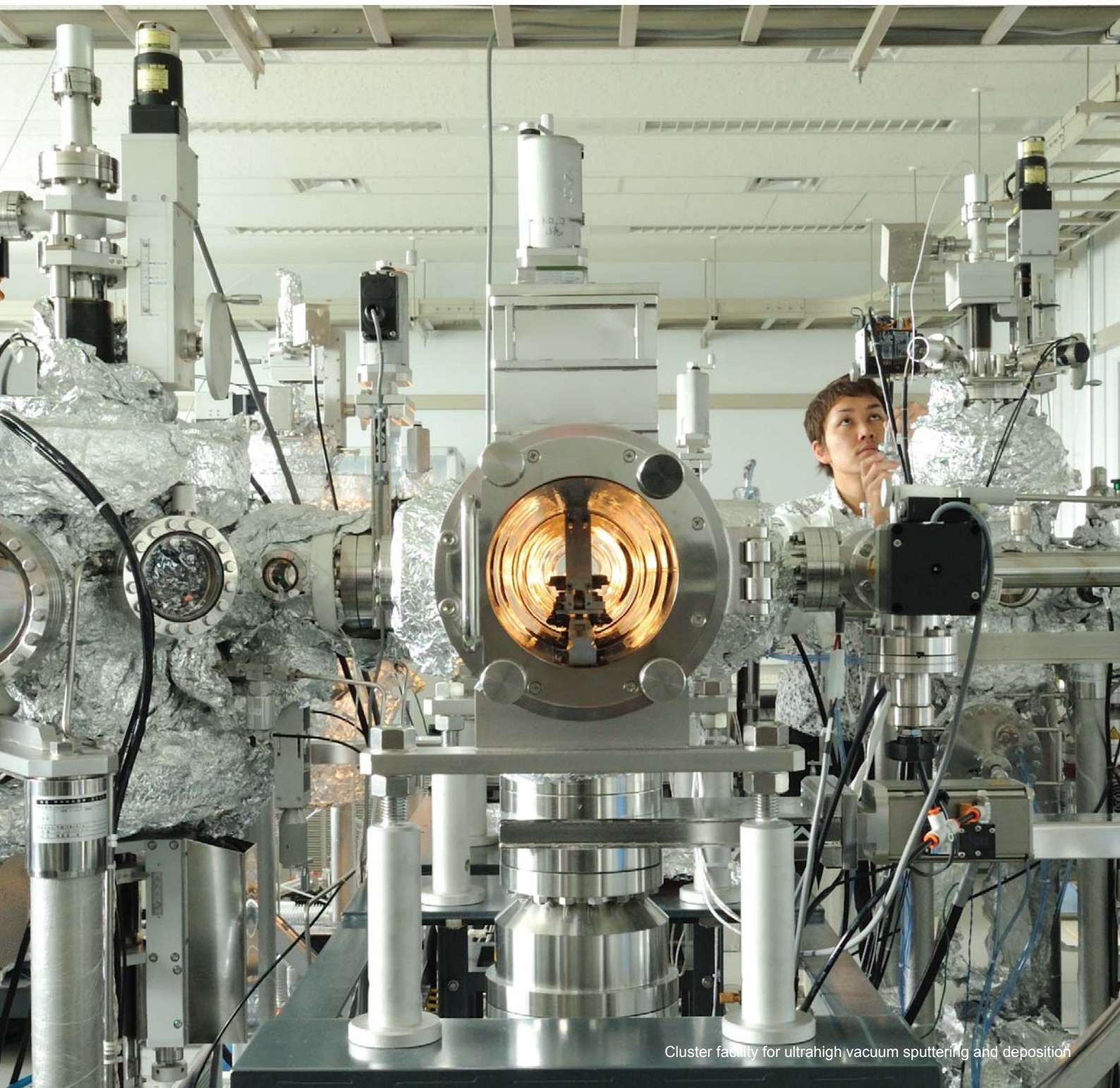
# NIMS

*2010. October*

# NOW

## International

### **Magnetic Materials for Energy Saving**



Cluster facility for ultrahigh vacuum sputtering and deposition



# Magnetic Materials for Energy Saving

Permanent magnets are used widely in many application areas including motors, generators, air conditioners, hard disk drives (HDD), and cell phones. Among various permanent magnets, certain applications such as the traction motors for hybrid and electric vehicles, voice coil motors in HDD, and generators for wind mills require high performance permanent magnets based on neodymium, dysprosium, iron and boron. Both neodymium and dysprosium are rare earth elements, whose natural resources are relatively scarce. When nanosized magnets are densely dispersed in thin films, data can be stored by magnetizing these nanomagnets. This is what we know as HDD, which plays a critical role in modern data storage for recording television programs, movies and high definition images. The goal of our research at Magnetic Materials Center at NIMS is to develop high performance magnetic materials for energy saving and data storage.



## Development of High Performance Magnetic Materials by Nanostructure Control

Kazuhiro Hono, NIMS Fellow  
Managing Director, Magnetic Materials Center

### High performance permanent magnets

Permanent magnets are used for mechanical and electric power conversions such as electric power generators and motors, since they can generate magnetic field without supplying external energy. Induction motors and generators without permanent magnets will be large in size. Thus, these are not suitable for such applications as electric vehicles and wind power generators, where small size, light weight and high efficiency are essential. By using high performance neodymium based permanent magnets, these devices can be reduced in size and improved in energy efficiency, which leads to substantial energy saving.

### Permanent magnets in hard disk drives

The number of annual sales of hard disk drives (HDD) reached 800 million last year, which exceeded the number of sales of television sets and personal computers. Hard disk drives (HDD) are used in large quantity in high definition television (HDTV) recording and computer data storage. In these applications, magnetic particles with a diameter of 6 nm are densely dispersed with a certain crystallographic orientation on the surface of a disk. The bit information is recorded by changing the S/N directions of these nanomagnets. In HDDs, the magnetic information is read by a head which senses the magnetic fields while the disk rotates at a high speed. Neodymium magnets are also used in ultra-small spindle motors which rotate HDD disks and in voice coil motors (VCM) which actuate the heads. In other words, higher densities and greater miniaturization of HDD would have been impossible without neodymium magnets.

### Nanomagnets for data storage

Co-Pt-Cr alloys are currently used as the nano-sized particles of the recording media for HDD. However, to increase the recording density to more than twice the current level (~550 Giga bit per square inch (Gbps)), FePt alloys with the magnetocrystalline anisotropy of an order of magnitude larger than the Co based alloy must be used for the recording media.

### Spintronics applied in hard disk heads

The giant magneto resistance (GMR) devices that had been used as read heads of HDD are made from stacks of nanosized ferromagnetic layers and nonmagnetic spacer layers, and their magnetic resistance changes depending on the relative directions of magnetization of the ferromagnetic layers. The discovery of this GMR led to the evolution of the field called "spintronics", in which electrical current is controlled by the direction of spins of ferromagnets. GMR devices were put into the practical use as read heads of HDD only 10 years after this discovery.

The current read heads use tunneling magneto resistance

(TMR) devices, where small changes in the magnetic field induce large changes in electrical resistance. However, as the recording densities of HDD approach 2 Tbps, the TMR devices that use insulator as a spacer layer is expected to become incapable of responding to the fast signal rates due to their intrinsically high electrical resistance. Therefore, research to achieve high magnetoresistance output with low resistance GMRs and the development of completely new types of magnetic sensors are underway.

### Potential of magnetic memory

HDDs have a low bit price, and therefore are suitable for huge data storage. Dynamic random access memory (DRAM) that store information by charges in condensers are used widely for the work memory of computers. However, DRAM is a "volatile" memory, that is, the data will be lost by the discharge of the stored charge when electric power is shut down. Therefore, data must be stored to DRAM again from HDDs when the computer is started up.

Magnetoresistive random access memory (MRAM) is a new type of memory which uses TMR devices in information storage. This is a nonvolatile memory, which means that the data are retained by magnets even if the power is shut down. Although high expectations are placed on MRAM as the work memory for instant-on computers, the potential of these devices is not only limited to applications such as work memory, but may be used for data storage like HDD, if high density and low cost MRAM can be developed in the future. Since MRAM does not need to rotate a disk at high speed for data storage, wider application of MRAM may lead to an enormous energy saving in the IT field.

As outlined above, the goal of the magnetic materials center is to develop high performance magnetic materials such as rare earth permanent magnets, soft magnetic materials, magnetic recording media, magnetic sensors for read heads, and spintronics devices by controlling the nanostructures of ferromagnetic materials. The materials innovation in magnetic materials will lead to substantial contribution in energy saving.

**Kazuhiro Hono** obtained a Ph.D. degree in Metals Science and Engineering at the Pennsylvania State University. Previous positions include Post Doctoral Research Associate at Carnegie Mellon University (1988-1989) and Research Associate at Institute for Materials Research, Tohoku University (1990-1995). Appointed as Senior Researcher, National Research Institute for Metals (NRIM; now NIMS) in 1995. Present position as a Fellow of NIMS since 2004 as well as Managing Director of the Magnetic Materials Center since 2006. Also, Professor of Materials Science and Engineering, Graduate School of Pure and Applied Sciences, University of Tsukuba.



## Material for Higher Density Hard Disk Drive

### Development of Thermally Assisted Magnetic Recording Medium Using L1<sub>0</sub>-FePt

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#### Toward hard disk drive with high density and capacity.

With the rapid increase of the storage capacity due to the promulgation of digital instruments like digital camera, and digital TV, there comes up more and more demand on even higher density recording devices. In current storage system, the most popular structure is the hard disk drive (HDD) due to high reliability, low cost and high density. It is essential to improve the recording density and performance in HDDs.

The areal density of the current commercial HDD is about 540 Gb/in<sup>2</sup>, which corresponds to a single bit size of 35 nm and each bit contains 15 CoPtCr grains. To increase the areal density to 1 Tbits/in<sup>2</sup> and above, the dimension of a single magnetic particle has to be reduced to 4 nm. However, when we decrease the grain size to 4 nm, the magnetization could be flipped randomly by thermal agitation at room temperature. This is called superparamagnetic effect, the main obstacle in further increasing the density in magnetic recording media. For current recording media in commercial products, the limitation is about 2 Tbits/in<sup>2</sup>.

#### Thermal Assisted Magnetic Recording.

L1<sub>0</sub>-ordered FePt alloy has been received much attention as a thermally stable nano-size magnet, since the magnetocrystalline anisotropy of L1<sub>0</sub>-FePt is one order higher than that of CoPtCr alloy.

However, L1<sub>0</sub>-FePt has a big problem in the application point of view. Due to high magnetocrystalline anisotropy, a write field of 30 kOe is required to switch the magnetization of FePt nano-particles. The write head in current commercial HDDs cannot be applied in FePt media. To solve the problem, thermal assisted magnetic recording (TAR) has been initiated to realize the recording density of 4 Tb/in<sup>2</sup> and above. In TAR, low field write process is feasible because the area to be recorded will be heated up to around its Curie temperature, at which the magnetization is reduced so that a reasonable low field is sufficient to flip the magnetization. After

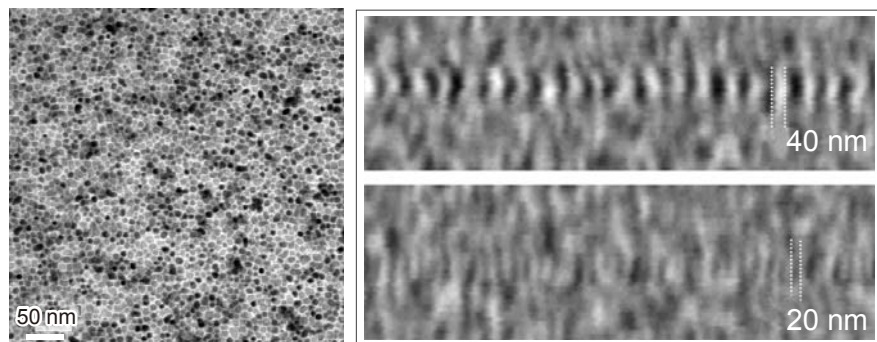


Fig. TEM image (left) of a FePtAg-C granular thin film, and static test result (right). Photographs courtesy of Hitachi Global Storage Technologies San Jose Research Center.

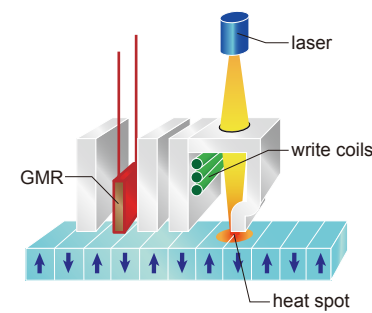
writing at high temperature, the magnetic domain is formed and the medium is cooled down to room temperature to facilitate the read-back process and long-term storage.

To apply L1<sub>0</sub>-FePt as a qualified TAR medium, it is necessary to realize L1<sub>0</sub>-FePt nano-particles with a size of 4 nm and size distribution of less than 10%, and perfect c-axis alignment as well.

To obtain this film structure, we co-deposit Fe, Pt, Ag and C on a thermally oxidized silicon substrate in an ultra-high vacuum chamber. We succeeded in the growth of FePtAg-C nanogranular film with the average grain size of 6.1 nm and size distribution of 1.8 nm. This film has an extremely high coercivity (H<sub>C</sub>=37kOe) with excellent thermal stability.

A static write test using TAR head on this film was carried out by our collaborators in Hitachi Global Storage Technologies. Through demonstration, 20 nm bit length can be clearly observed in Fig.2. More detailed analysis revealed that a maximum density of 450 Gb/in<sup>2</sup> can be achieved. As of October 2010, this is the world record for the areal density in TAR mode.

In the future, even higher densities are expected to be possible by refining the average grain size to 4 nm, further narrowing size distribution, and improving the medium structure in consideration of the heat transfer during the TAR process.



Thermally assisted magnetic recording

**Yukiko Takahashi** (Dr.Eng.) Completed Doctor course at Graduate School of Tohoku University. After served as Fellow Researcher at Japan Society for the Promotion of Science, joined NIMS Magnetic Materials Center. Senior Researcher at Magnetic Materials Group from 2010.

**Li Zhang** After completing Ph.D course at Carnegie Mellon University, joined University of Electric Science and Technology of China and Hokkaido University in 2005, and Postdoctoral at NIMS from 2008.

Curie temperature: Fe, 770°C, Ni (nickel), 354°C.

Perpendicular magnetic film: A magnetic film for the perpendicular magnetic recording method. In the perpendicular magnetic recording, the medium is magnetized in the perpendicular direction. Another recording method previously used is longitudinal magnetic recording in which the medium is magnetized in the in-plane direction.

## Development of CPP-GMR Devices Using Heusler Alloys

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#### Spintronics – A highly promising field.

Electrons in materials have electric charge, which carries electric current. At the same time, electrons behave as small magnets and therefore, materials also show “magnetism.” Each electron has a property called “spin,” which determines the direction of the magnetization of each electron to be upward (up-spin) or downward (down-spin). The technology of combining and utilizing the two properties of electrons, charge and spin, is called “spintronics.”

A half-metal is a material where electrons with only one spin direction are metallic and contribute to the electrical conduction. Electrons with the other spin direction carry no current like in an insulator. Thus, a half metal is expected to have large effects in a variety of fields of spintronic applications because it can be a source of conduction electrons with the perfectly aligned spin direction.

When a metallic thin layer with a thickness of several nanometers or less is sandwiched between two ferromagnetic thin layers, the electrical resistance of the film changes dramatically depending on the mutual direction of the magnetizations of the two magnetic layers, parallel or antiparallel. This phenomenon is called Giant magnetoresistance (GMR), one of the most important applications of spintronics.

#### Expectations for higher recording density and CPP-GMR.

A hard disk drive is equipped with a read head, which converts magnetic field generated by the recording pattern to an electrical signal. GMR has been applied to read heads, making an important contribution to higher recording densities.

The current read heads mostly uses tunneling magnetic resistance (TMR), in which an insulating thin layer, or “spacer,” is sandwiched between ferromagnetic layers. In order to realize even higher recording densities, however, devices which display large resistance changes with small resistance and devices which generate microwaves are required.

Therefore, focusing on CPP-GMR, which is a type of GMR characterized by an electric current flow perpendicular to the film plane (CPP: current perpendicular to

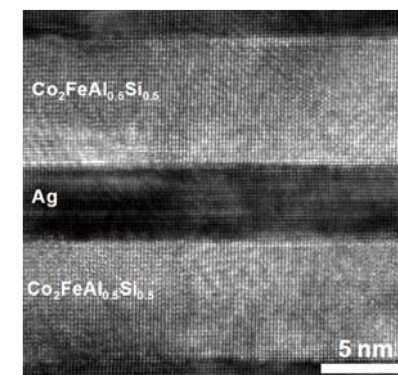


Fig. 1 Cross-sectional transmission electron microscope image of a CPP-GMR device.

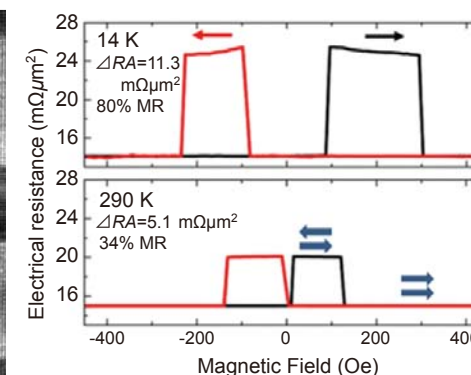


Fig. 2 Magnetic field dependence of magnetoresistance at room temperature and low temperature.

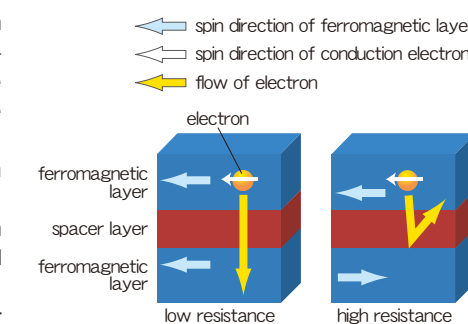
plane), we have been engaged in research using Heusler alloys, which have a promising half-metallic property as a substitute for conventional CoFe alloys, etc. in the ferromagnetic layer.

Heusler alloys have the composition formula X<sub>2</sub>YZ with a regular atomic arrangement called the L<sub>21</sub> structure. Both theoretically and empirically, it is expected that a number of alloys are half-metals.

We fabricated devices using Heusler alloys such as Co<sub>2</sub>Fe(Al<sub>0.5</sub>Si<sub>0.5</sub>) as the ferromagnetic layer and silver (Ag) as the spacer layer. As shown in Fig. 1, these devices have a flat layered structure at the atomic level. In work to date, we have obtained magnetic sensitivity (magnetoresistance variation) of 34% at room temperature and 80% at cryogenic temperature (Fig. 2). These are the highest values obtained with CPP-GMR.

It is also advantageous for realizing micro-devices for achieving high recording densities that a large magnetoresistance effect can also be obtained with extremely thin (2.5nm) ferromagnetic layers. However, at the present time, it is thought that satisfactory performance at room temperature is still not obtained, even with these values, because the atomic order in the alloy is not sufficient.

In the future, our aim is to develop new materials with higher performance and realize higher magnetic sensitivity by optimizing the preparing conditions, and to study the potential of devices based on these innovations for use in high density magnetic recording heads.



Schematic figure of GMR

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## NIMS Materials Research Contributing to Magnetic Random Access Memory (MRAM)

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**MRAM devices require the TMR of high output magnetic tunnel junctions.**

Hard disk drives (HDDs) are actively used as large capacity storage devices. On the other hand, the nonvolatile memories of solid-state devices without a drive section has also become indispensable. As future applications, the main aims are the replacement of some HDDs for data storages, and the realization of higher speeds and lower power consumption in the system as a whole by the development of hybrid devices which include logic circuits.

At present, semiconductor-based flash memories are the representative type of nonvolatile solid-state memory, but these devices have weaknesses in terms of operating speed and the maximum number of rewrite cycles. MRAMs have attracted attention as a new solid-state nonvolatile memory which overcomes these problems.

The first-generation MRAMs used a GMR effect. Today, however, the TMR effect in magnetic tunnel junctions (MTJs) is used due to their high output. A 16 Mbit-scale MRAM has already appeared in the market, but to acquire a large market, the development of gigabit class products is necessary. To achieve this, technical development to realize high integration is currently in progress.

The first problem which arises when the recording magnetic layer is miniaturized accompanying higher integration is that magnetic writing becomes difficult. To solve this problem, practical application of writing by "current-induced magnetization reversal" is essential.

The second problem is the thermal stability of the magnetization of the recording layer. Because the magnetization of small magnetic substance is disturbed by thermal energy, it is necessary to induce relatively large magnetic anisotropy so that the direction of magnetization (recording) is not changed by this thermal fluctuation.

The countermeasures for these problems are considered to get higher efficiency in current-induced magnetization reversal in MTJ, and to adopt the perpendicularly magnetized systems in which magnetic anisotropy has relatively little effect on spin injection-induced magnetization reversal. In both cases, "materials" are expected to play an important role. For the former countermeasure, the development

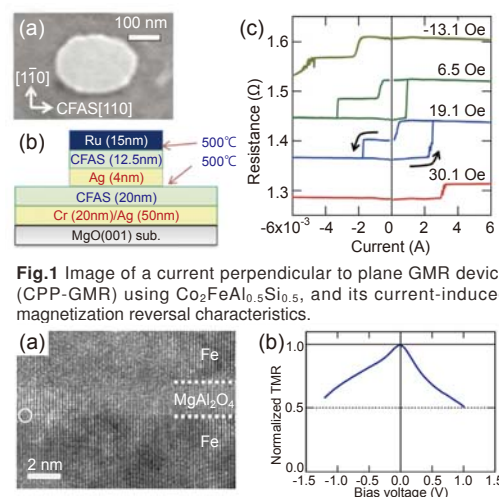
of a highly spin-polarized material and high quality tunnel barrier material and control of the interfacial structure of these materials are important. For the latter, the key is research on perpendicular magnetic anisotropy in thin film materials, which have been subjects of study for many years as medium materials for magneto-optical recording and perpendicular magnetic recording, based on the new viewpoint and conditions of application to MRAMs.

**NIMS materials research provides the route to solutions.**

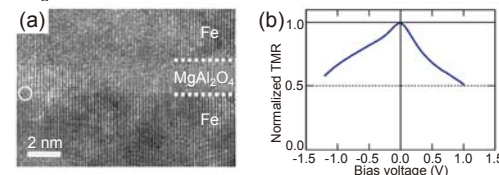
NIMS researchers have an extensive record of achievements in the development of cobalt (Co)-based Heusler alloys, which are high spin-polarized materials, including a huge TMR effect in a  $\text{Co}_2\text{FeAl}$  alloy (room temperature: 330%, cryogenic temperature: 700%). In addition to the high spin polarization, the Heusler alloys also have a small damping constant of magnetization, and thus are effective for realizing high efficiency current-induced magnetization reversal.

**Fig.1** shows the demonstration of current-induced magnetization reversal with a Heusler alloy for the first time in the world. Because this was an experiment with a GMR device, direct comparison with the results for tunnel junctions and direct practical application are not possible. However, this experiment demonstrated that the current density for magnetization reversal is smaller than with the conventional alloy, as a value of  $9.3 \times 10^6 \text{ A/cm}^2$  was obtained as the threshold current density.

Recently, NIMS also succeeded in creating a novel material system for use as a tunnel barrier material. At present, the standard barrier material is crystalline magnesium oxide (MgO). However, the mechanism responsible for large TMR is not fully understood. Related to this, the problem that the properties of MgO barriers tend to be dependent on growth conditions (equipment) remains to be solved. Therefore, from both the viewpoint of understanding the MgO barrier and the viewpoint of studying the possibility of substitutes, a search was carried out for crystalline barrier materials other than MgO. As a result, room temperature TMR exceeding 200%



**Fig.1** Image of a current perpendicular to plane GMR device (CPP-GMR) using  $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ , and its current-induced magnetization reversal characteristics.



**Fig.2** (a) Cross-sectional TEM image of the newly-developed  $\text{Fe}/\text{MgAl}_2\text{O}_4/\text{Fe}$  tunnel junction, and (b) its bias voltage dependence of TMR.

was realized with  $\text{MgAl}_2\text{O}_4$  (spinel), which has a different crystal structure from MgO.

Because spinel has small lattice mismatch with iron and iron alloys, it is considered a promising material for the manufacture of MTJ with few interfacial defects (misfit dislocations). In tunnel junctions using iron alloys in the top and bottom electrodes, an interface with virtually no misfit dislocations is formed, as shown in **Fig.2(a)**. **Fig.2(b)** shows the bias voltage dependence of TMR in this junction. This property is superior to that obtained with the standard material system of  $\text{CoFeB}$  electrodes/MgO barrier.

Because the magnetic tunnel junction is the basic element of MRAMs, we are also engaged in research and development for extension of the material system and development of double junction tunnels, with the aim of improving properties and adding new functions to these devices.

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**Shinya Kasai** (Dr.Sci.) Completed doctoral degree in the Graduate School of Fundamental Science and Technology at Keio University in 2004, and held a position as Assistant Professor at Division of Nanospintronics, Institute for Chemical Research, Kyoto University prior to joining NIMS in present position as Researcher in 2009.

**Seiji Mitani** (Dr.Eng.) Completed doctoral course in Materials Science at Nagoya University. Previous positions include Research Associate at Institute of Materials Research, Tohoku University (1993-2001), Associate Professor at the same Institute (2001-2008), and Researcher at NIMS (2008). Appointed to present position in 2009.

**Current-induced magnetization reversal:** Phenomenon in which the direction of magnetization changes depending on the transfer of spin angular momentum from conduction electrons to magnetization when a spin-polarized current passes through a magnetic nanostructure. This is a relatively new physical phenomenon which was predicted theoretically in the mid-1990s and demonstrated in 2001. Like GMR, it has attracted attention for the short period from its discovery to the development of applications. MRAMs utilizing the spin injection method are also called spin-RAMs.

## Novel Logic Device Performs Logic Operations Using Only Spin

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**Spin-based logic devices.**

In addition to providing the higher performance necessary to support ongoing progress in information and communications technology (ICT), logic devices must also contribute to energy saving. Among various approaches to reducing power consumption, hybrid devices which include both logic circuits and nonvolatile memory are expected to reach practical application in the near future. However, active R&D is also underway on more advanced devices, in which a nonvolatile memory function is incorporated in the logic circuit itself. One example of these advanced devices is called spin MOS-FET. This type of device uses ferromagnets in the source and drain electrodes.

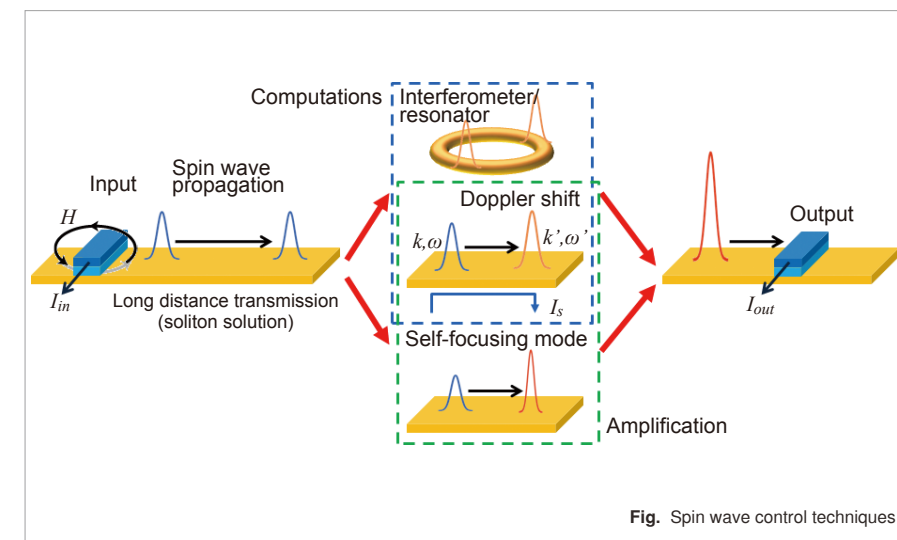
An even more ambitious approach is a new class of magnetic logic devices in which the logic operations are performed using only the magnetic function, in other words, spin. Logic devices using spin positively utilize the fact that spin is a different physical quantity from charge. As spin is a vector quantity, various spin control methods other than use of a magnetic field have been proposed, including use of electrical current and the spin orbit interaction. High expectations are placed on the development of these various logic device architectures.

NIMS is engaged in research on the dynamic properties of spin and magnetic moment, or "spin dynamics," which forms the fundamentals for magnetic logic devices. NIMS researchers are investigating the spin dynamics in an external magnetic field or electrical current, and are developing techniques for its control. These phenomena include spin waves, which resemble ripples of magnetization in a ferromagnet, magnetic domain walls, which are the interfaces between magnetization states in magnetic substances, and others.

Figure is a diagram which enumerates in concrete form the control techniques related to spin waves, showing a schematic representation of how spin waves undergo various operations, including amplification, and are converted to current.

**The search for the motion of magnetic domain walls – the places where spin direction changes.**

A variety of studies have been carried out on the motion of magnetic domain



**Fig.** Spin wave control techniques

walls, and researchers are searching for the optimum material for moving domain walls by electrical current, in other words, current-driven domain wall motion. However, because the mechanism of current-driven domain wall motion has not been adequately elucidated, guidelines have not been obtained for materials development.

Therefore, basic research on the domain wall motion is also underway. As one example, NIMS researchers recently established a new technique for detecting magnetic domain wall motion in nanowires. This technique is based on detection of the stray magnetic field of nano regions. As advantages of this method, unlike conventional electrical measurements, measurements do not affect the motion of the magnetic domain walls, and this technique has excellent sensitivity to high speed motion of domain walls, which will be critically important in the future.

Where magnetic logic devices are concerned, this R&D on spin dynamics is still in the exploratory stage. However, magnetic dynamics is also extremely important for reducing magnetic head noise and for magnetic memory writing operations. For this reason, active research on spin dynamics is in progress in countries around the world.

**Future development.**

As future research on magnetic logic devices, research on energy conversion in devices and the interaction between

light and spin is also planned, as mutual conversion of magnetization states and magnetization motion with electric current and light will become even more important in the future as a means of realizing various inputs and outputs in logic devices and transmitting information between logic devices.

Because the electrons responsible for electrical current have spin polarization, and circularly polarized light has spin, magnetism and electrical current, and magnetism and light are considered to have good compatibility.

**Masamitsu Hayashi** (Ph.D.) Completed Doctoral course in the Materials Science and Engineering at the Graduate school of Stanford University in 2007. Held a position at IBM Almaden Research Center as Research Fellow in the same year, and current position from 2008.

**magnetic domain walls:** regions in which spin is oriented in the same direction are called magnetic domains, and the boundaries between these domains are called magnetic domain walls.



## Toward the Development of High Coercivity Dysprosium Free Permanent Magnets

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The Nd-Fe-B type permanent magnets, which exhibit excellent hard magnetic properties, were discovered about 25 years ago. Since that time, many researchers have been working to improve hard magnetic properties of these magnets. The Nd-Fe-B type permanent magnets are widely used in different application specifically electro-mechanical applications in different types of motors. However, the coercivity of the sintered magnets (~10 kOe) is only 14% of the anisotropy field (~75 kOe), which is too low for certain applications like traction motors for hybrid and electric vehicles. The current Nd-Fe-B high coercivity sintered magnets for hybrid and electric vehicle applications contain approximately 40% of Dy with respect to the entire rare earth elements to increase the coercivity to the level of 30 kOe. However, due to high cost and limited natural resources for Dy, developing high coercivity Nd-Fe-B permanent magnets without using Dy is indispensable.

To understand the reasons of low coercivity for Dy free Nd-Fe-B magnets, we performed multi-scale microstructural analysis on different types of Nd-Fe-B sintered magnets from the micro- to the nano-scale, using the focused ion beam scanning electron microscope (FIB-SEM), transmission electron microscope (TEM), and a laser-assisted 3-dimensional atom probe (La3DAP) developed at NIMS as complementary analytical techniques. In this research, we clarified the responsible microstructural factors for low coercivity of Nd-Fe-B type permanent magnets which had not been studied before. In joint work with a magnet manufacturer, we also carried out a study of microstructure modification with different processing routes and addition of different elements.

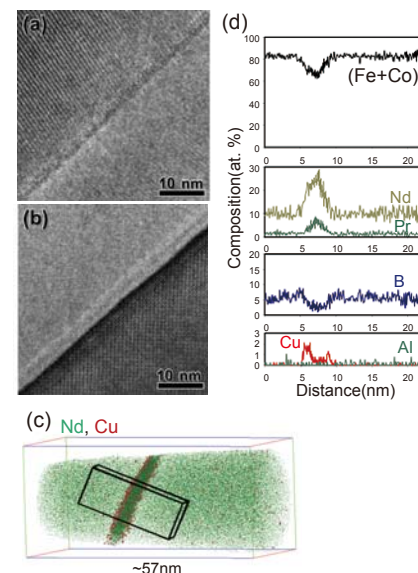
In commercial sintered magnets, it is known that coercivity can be improved by 20% or more with trace addition of specific elements such as Cu and post sinter heat treatment. In the Nd-Fe-B type permanent magnets, grain boundary phase plays an important role in coercivity enhancement with isolating the Nd<sub>2</sub>Fe<sub>14</sub>B grains as well as pinning of domain wall during motion in demagnetization process leading to enhancement of coercivity. Our quantitative and qualitative multi-scale microstructural analysis showed the structure, and compo-

sition of an existing grain boundary phase surrounding the main Nd<sub>2</sub>Fe<sub>14</sub>B phase, as shown in Fig.1. This suggested that coercivity can be increased by reducing magnetic coupling of the main phase by forming the grain boundary phase containing Nd and Cu with a thickness of several nanometers.<sup>1,2)</sup> Although it was known that coercivity can be increased by reducing the grain size of the Nd<sub>2</sub>Fe<sub>14</sub>B phase, conversely, coercivity decreases if the grain size is reduced to less than approximately 3 μm. The results of a microstructural analysis showed that the cause of this problem is an inadequate supply of Nd to the grain boundaries due to formation of neodymium oxide phase as isolated grains.<sup>3)</sup> Based on this result, a magnet manufacturer which was our partner in this joint research implemented countermeasures to reduce oxygen and is now achieving high coercivity with finer grains.

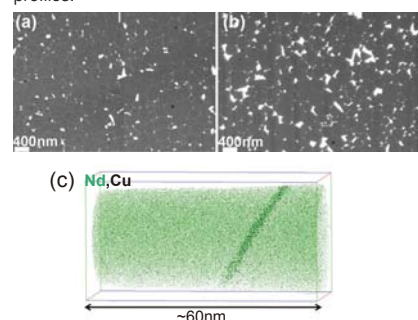
On the other hand, with applying HDDR (hydrogenation-disproportionation-desorption-recombination) process on Nd-Fe-B powders (with the particle size of between 50-300 μm), ultrafine grain size (~250nm) with very high crystallographic texture of Nd<sub>2</sub>Fe<sub>14</sub>B grains along the easy axis direction of the initial monocrystalline can be obtained. Ultra-fine grain size that is 10 times smaller than that of sintered magnets makes these materials promising for producing high coercivity permanent magnets. In spite of the grain size reduction, the coercivity of HDDR magnet is still comparable to that of sintered magnets. The reasons for low coercivity in HDDR processed powders were investigated. The HDDR powders were found to have thinner grain boundary phase containing lesser non-magnetic elements compared to the sintered magnets.<sup>4,5)</sup> This understanding inspired us to modify the chemistry of the grain boundary phase with diffusion of low melting point Nd-Cu alloy to the grain boundaries of the HDDR processed powders which have resulted in achieving the highest value of coercivity (19.5 kOe) for Dy free HDDR powders (Fig. 2).<sup>6)</sup>

In order to obtain even higher coercivity, it is extremely important to clarify the relationship between the microstructure and properties of the material and apply appropriate control to the microstructure, as

exemplified by this work. We hope to contribute to this effort with advanced multi-scale microstructural analysis techniques.



**Fig.1** TEM images of specimen (a) before diffusion treatment (9 kOe) and (b) after annealing at (11.8 kOe). (c) Nd and Cu atom map around grain boundary in annealed specimen, and (d) the composition profiles.



**Fig.2** SEM backscattered electron images of specimen (a) before diffusion treatment (16 kOe) and (b) after diffusion treatment (19.6 kOe). (c) Nd and Cu atom map around grain boundary in diffusion processed specimen.

**Tadakatsu Ohkubo** (Dr. Eng.) Previous positions include Research Associate at Nagaoka University of Technology (1992-1994), Research Associate at Osaka University (1994-2002), and Senior Researcher at NIMS (2002-2006). Appointed to present position as Group Leader, Nanostructure Analysis Group, Magnetic Materials Center in 2006. Also been a Visiting Professor in Tokyo University of Science since 2008.

**Hossein Sepehri Amin** Currently enrolled in the Doctoral Program in Materials Science and Engineering (D3), Graduate School of Pure and Applied Science, University of Tsukuba. NIMS Junior Researcher.

## Defects Play a Key Role in Sensor Materials Development

Hajime Haneda

Managing Director, Sensor Materials Center

The Sensor Materials Center is engaged in research aimed at elucidating the functions of substances which are capable of detecting (sensing) disasters and hazardous materials, and developing new sensor materials. In this FACE Interview, the Center's Managing Director, Dr. Hajime Haneda, discusses the fascination of sensor materials research and the image of the ideal researcher.

— Have you always been interested in sensors?

Yes. But rather than saying I'm an expert in sensors, I am personally interested in the defect structures which exist in solids. Sensor materials, and particularly chemical sensors, are an extremely attractive object of study because defect structures at the surface and defects of the bulk are closely related. I selected this because it's an attractive field for applications.

— What is your reason for working with defects?

As a joke, I say it's because I'm a defective person, but in any case, not that many types of ceramics have a long history of use. Practically speaking, since they have come to be called fine ceramics, this perhaps means alumina (sapphire), perovskite, and zinc oxide. However, their range of applications is extremely large. To explain why this is so, in many cases, this depends on the microstructure or defect structure as well as the properties of the bulk substances. Accordingly, in the search for substances and materials of these types, the target of research is not limited to the bulk, but also includes the microstructure and defect structure.

I'm attracted to that general area, and have been working in the field for 35 years. In my case, the range of defects is small. I'm involved in work on oxide materials and the diffusion of anions in those materials. In other words, I have spent 35 years working only on the diffusion of oxygen.

— What has impressed you in research to date?

The measurement of non-equilibrium defects. It is a so-called heresy, but these defects frequently occur in actual materials. Non-equilibrium defects are difficult to measure because they change in the course of

measures. You can't measure them if you don't produce the material yourself. I have made and measured various materials, but I was impressed when I made transparent ceramics. I succeeded in realizing a laser oscillation by reducing the pore size to below the PPM level. Normally, high quality single crystals are used as laser host material, but because single crystals crack easily, at this time, polycrystalline materials were used. Since polycrystals are suitable for producing large materials, I was able to produce a high output laser, and also succeeded in simulation of nuclear fusion.



— What do you do in your free time, when you're not engaged in research?

During the 35 years of my life as a researcher, I played soccer for 20 years in my younger days. I had to choose among baseball, soccer, and tennis, and I chose soccer. For around 10 years I was the youngest member, so I played forward. When I became captain, I played sweeper and other positions that people don't like. In any event, assembling a team is really difficult, and it was hard work to find 11 people so we could enter league play. Still, I enjoyed the drinking parties after games, and I've continued that right up to the present.

— What are your feelings about the young people of today?

They don't like to drink together, the way my generation does, and they aren't very communicative. People my age, who like a lot of noise and excitement, feel that there's something slightly missing. And young people work seriously when they're told to do something, but they don't act if they aren't told what to do.

In a sense, a researcher can spend his or her entire life in play, so if a person can do only one big job that makes a contribution to the human race as a whole, I believe that is one way of living. Be tenacious over the long-term span, regardless of what others think of you.

— That's particularly applicable to national research institutes like NIMS, isn't it?

It certainly is. If a national research institute sets one target, everyone tends to move in that direction. This is very important, but as a result, there is a tendency to be rootless, and to waste the accumulation of many years. In the progress of technology, the accumulation of past achievements is necessary, and it is difficult to start from zero when beginning a new project. I want to strike a good balance between the two.

**Hajime Haneda** (Dr. Eng.) After graduating Department of Applied Chemistry School of Engineering Yokohama National University, joined National Institute for Research in Inorganic Materials (NIRIM) as a researcher. After serving as Director of Electroceramics Group at NIMS, current position as Managing Director of Sensor Materials Center from 2006.

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**Bulk:** In materials and specimens, "bulk" means a solid body or aggregate of a substance of a certain size.



## New Cellular Metal Materials – Encapsulation of Polymers and Ceramics –

Satoshi Kishimoto

Composites Group,  
Hybrid Materials Center

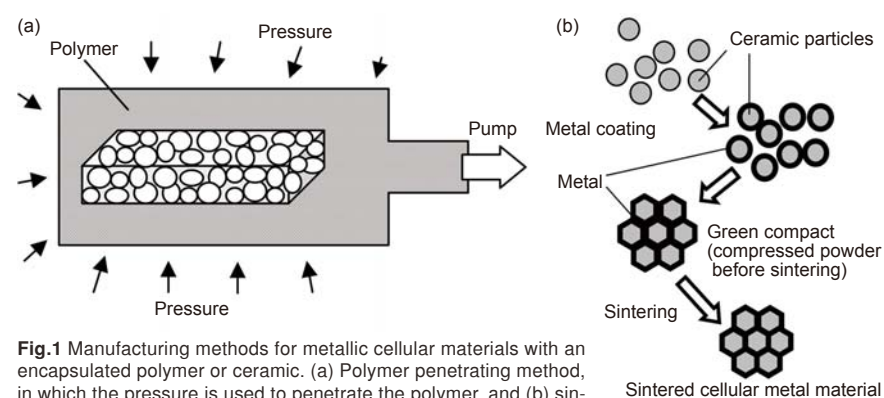
Cellular materials are sponge-like materials which contain tiny spaces, or pores, with high porosity. Metallic Cellular materials are produced by various methods, including foaming of the metal, solidification of numerous hollow metal spheres, baking of metal powder to a sponge-like form, and plating metal in polymer sponge materials in which spaces already exist.

Due to their distinctive form, cellular materials are light in weight relative to their volume, and are also capable of shock absorbing. Taking advantage of these features, they are used in materials which soften the impact of accidents on the human body (and particularly the skull), for example, by use as spacers between the bonnet and engine in automobiles. It is also possible to improve the bending strength of hollow pipes and similar parts by filling these components with cellular materials.

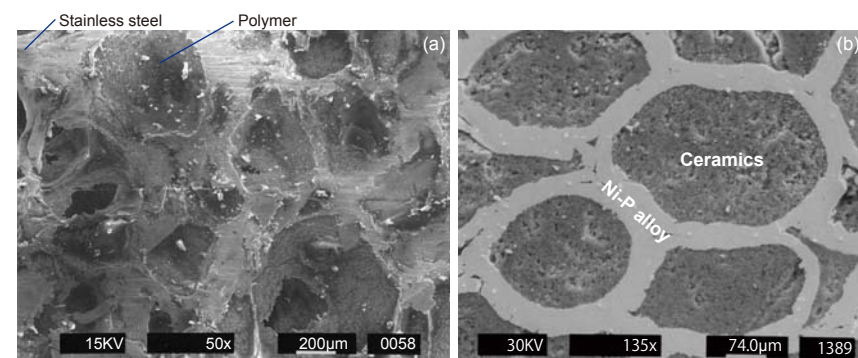
We developed a technique for encapsulating materials (polymers, metals, or ceramics) which are different from the metal of the cell walls into the cells (spaces) in the materials which have this cellular structure.

When encapsulating a polymer, the material is manufactured by impregnation of the polymer into metallic open-cell cellular material in which the cells are interconnected, as illustrated in **Fig.1(a)**. Ceramics are encapsulated by coating a metal on porous ceramic particles, followed by sintering, which results in mutual bonding of the metal (**Fig.1(b)**). Scanning electron microscope images of metallic cellular materials with an encapsulated polymer or ceramic produced in this work are shown in **Fig.2**. **Fig.2(a)** shows a stainless steel cellular material with an encapsulated polymer, and **Fig.2(b)** shows a stainless cellular metal material with an encapsulated ceramic.

When a metallic cellular material does not contain any encapsulated substance, the material is extremely lightweight, as mentioned above, but if its porosity is increased, strength decreases drastically. For



**Fig.1** Manufacturing methods for metallic cellular materials with an encapsulated polymer or ceramic. (a) Polymer penetrating method, in which the pressure is used to penetrate the polymer, and (b) sintering method, in which metal-coated ceramic particles are sintered.



**Fig.2** Scanning electron microscope images of metallic cellular materials. (a) Metallic cellular (stainless steel) material with an encapsulated polymer (polyurethane) and (b) metallic cellular material (Ni-P alloy) with an encapsulated ceramic (silicon carbide).

example, when density is reduced to 1/10, compressive strength decreases to 1/100 that of the original material.

To solve this problem, a dramatic increase in compressive strength can be achieved by encapsulating a polymer in the material. In particular, in low density (high porosity) materials, their strength can be increased by more than ten times. Even considering the weight of the encapsulated polymer, specific strength<sup>\*1</sup> can be increased by more than twice. Furthermore, its properties can also be improved.

In the case of metallic cellular materials with encapsulated ceramics, it is possible to produce materials which possess

the functions of ceramics and the strength of metal, particularly if functional ceramics<sup>\*2</sup> are encapsulated.



**Satoshi Kishimoto** (Dr. Eng.) Joined NRIM in 1984. Assigned as Senior Researcher at NRIM in 1993. Senior Researcher at NIMS in 2001. Current position from 2009.

<sup>\*1</sup> Specific strength: Value of strength-to-weight ratio, with the same weight, larger values indicate higher strength.  
<sup>\*2</sup> Functional ceramics: Ceramic which have functional properties, such as titanium dioxide, which has a catalytic function.

## Iron-based Superconductivity Induced by Alcoholic Beverages

Yoshihiko Takano

Group Leader, Nano Frontier Materials Group,  
Superconducting Materials Center

Keita Deguchi

Nano Frontier Materials Group,  
Superconducting Materials Center

Triggered by the discovery of the iron-based superconductor LaFeAsO in 2008, an active search for new superconductors is now underway. In order to develop new superconductors, we were also focusing our attention on FeTe, which has a crystal structure similar to that of iron-based superconductors.

Because FeTe is a substance with antiferromagnetic ordering, it does not display superconductivity. In order to eliminate this antiferromagnetic ordering, which is thought to be an obstacle to superconductivity, we attempted to compress the lattice by doping with sulfur (S), which has a small ionic radius.

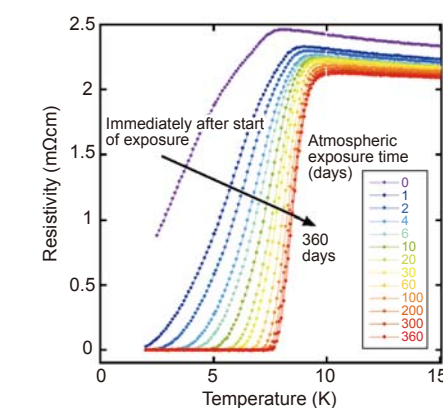
When we prepared a specimen of FeTe<sub>0.8</sub>S<sub>0.2</sub> with 20% S doping using the solid state reaction method, the antiferromagnetic ordering was eliminated, as aimed, but unfortunately, the specimen did not display superconductivity.

However, when the same specimen was measured one week later, surprisingly, it displayed superconductivity. In other words, it showed superconductivity as a result of exposure to atmospheric air.

**Fig.1** shows the temperature dependence of resistivity as a factor of exposure time, when the specimen was measured after exposure to the atmosphere for various periods of time. The specimen did not display zero resistance immediately after the start of exposure. However, zero resistance appeared after 1 day, and the superconducting transition temperature increased as the exposure period became longer.

In order to elucidate this mysterious phenomenon, we investigated whether superconductivity appeared when the specimen was placed in various environments. As a result, we discovered that this substance shows superconductivity in the presence of coexisting water and oxygen.

We considered that water might supply oxygen to the specimen acting as a catalyst, and tested various liquids seeking an effective catalyst for manifestation of superconductivity. For example, thinking that a liquid containing hydroxide (OH<sup>-</sup>) might



**Fig.1** The atmospheric exposure time dependence of superconducting transition temperature.

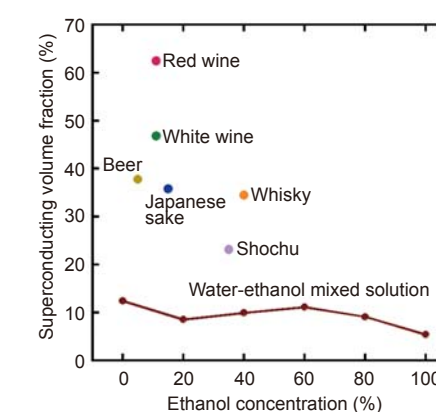
be effective, we tested ethanol and similar substances. Contrary to our expectations, the superconducting volume fraction was on the same order as with water.

Next, we attempted a similar experiment with various alcoholic beverages. We used alcoholic beverages because they are also aqueous solutions of ethanol and contain components which react with oxygen.

The beverages used in this experiment were red wine, white wine, beer, Japanese sake, whisky, and shochu. For comparison with these alcoholic beverages, we also immersed specimens in pure water, a mixed solution of water and ethanol, and anhydrous ethanol at 70°C for 24 hours.

**Fig.2** shows the superconducting volume fraction estimated from magnetic measurements. With the water-ethanol mixed solution, the superconducting volume fraction was small, at approximately 10%, and was independent of the alcohol concentration. In contrast, we found that the specimen immersed in red wine showed a value 6-7 times larger than that with the water-ethanol solution. The smallest value among the alcoholic beverages was obtained with shochu, but was still 2-3 times larger than with water-ethanol.

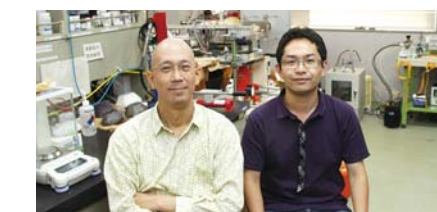
Based on the fact that large differences were observed in the superconducting volume fraction with red wine, white wine, and Japanese sake, which contain



**Fig.2** Superconducting volume fraction of specimens immersed in various alcoholic beverages at 70°C for 24 hours.

approximately the same concentrations of ethanol, it can be understood that some components of alcoholic beverages other than hydrous ethanol contributes to the manifestation of superconductivity.

At present, the authors are analyzing the composition of these alcoholic beverages in order to discover the key to the appearance of superconductivity with these substances.



**Yoshihiko Takano** (left) Dr.Sci. Completed doctoral course in the Department of Physics, Yokohama City University. In the same year, received a position as JSPS Research Fellow (PD) at the University of Tokyo ISSP, and so on. Joined NIMS in 1999. Group Leader of the Nano Frontier Materials Group from 2006 to the present. Also holds a concurrent position as Professor at the University of Tsukuba, Tokyo Univ. of Science and Tokyo Denki Univ. His specialties are the physics of superconductivity and magnetism, Josephson effect, high pressure science, diamond superconductivity, and the search for new superconductors.

**Keita Deguchi** (right) Entered the Graduate School of Pure and Applied Sciences of the University of Tsukuba in 2009. Currently in the 2nd year of the master's program and a NIMS Junior Researcher.

## NIMS New Partnership

(Oct. 8, 2010) The NIMS Quantum Beam Center and the Inter University Accelerator Centre (IUAC), India signed a memorandum of understanding (MOU) on joint research in connection with "Fabrication and Modification of Nano-materials by Ion Beams".

Visitors to the Accelerator Centre are impressed by a huge tower, standing 50 meters in height. This tower is actually the Centre's gigantic tandem accelerator, which is capable of generating a 200 MeV (200 million electron-volt)-class swift heavy ion beam. These swift heavy

ions rarely collide with the atoms in solids, but instead, cause strong electronic excitation in the nanometric cylindrical regions along the ion trajectories.

This joint research focuses on irradiation effects of the swift heavy ions on morphology and physical properties of nano-structures, such as metal and oxide nanoparticles dispersed in insulators. By combining the IUAC's 200 MeV-class heavy ion accelerator and the NIMS's advanced nanostructure characterization techniques, this project is expected to pioneer a new interdisciplinary region

which can be called "high-energy nano-technology."



From left: Dr. Devesh Kumar Avasthi (IUAC, Group Leader of Materials Science & Radiation Biology), Dr. Amit Roy (IUAC, Director), and Dr. Hiroshi Amekura (NIMS, Senior Researcher)

## Start of Operation of NIMS Researcher Database Service "SAMURAI"

On October 18, NIMS began operation of a comprehensive researcher database service which makes it possible to access the profiles, contents of research, list of publications, and other information on researchers affiliated with NIMS. In addition to tenured NIMS researchers, it is also possible to search and access various types of information for limited contract researchers such as invited researchers, research fellows, career-formation staff, and others, as well as engineering staff. The information which can be accessed includes the content of research, information on publications such as papers and books, information on patents, etc. Patent information covers published patents since 2004, and is linked to external sites based on Japan Patent Office electronic library data. The introduction of this service not only supports outreach by NIMS and referencing (citation) of NIMS-published papers, but is also expected to contribute to exchanges between researchers.



Image of the SAMURAI screen (Note: Screen is currently under development.)

## Hello from NIMS



In 2002, when I was a graduate student in Zhejiang University(ZJU) in China, my Chinese supervisor recommended me to NIMS with the financial support of a joint cooperative project. I met my Japanese supervisor in NIMS and started the most precious part of my academic journey. After receiving my Ph.D. from ZJU, I came back to work in NIMS as a postdoctoral researcher. The institute offers good research conditions for foreign researchers. I am engaged in the research of semiconductors and currently interested in the Si-based photovoltaic materials.



[Go skiing with friends at Zao Mountain]

Eight years has passed since I moved to Japan. I have become accustomed to living in this country, drinking ice water, eating sashimi, and Japanese style cooking. I enjoy the simple and peaceful country life here with some good friends. Cherry blossom viewing in spring, fireworks display in summer evening, maple excursion in autumn, mountain skiing in winter, those experiences and friendships I have made are special to me.

Jun Chen (Chinese)  
Researcher,  
Advanced Electronic Materials Center  
(2002/11-2004/04; 2005/09-present)



[At Tsukuba EXPO'85 Memorial Park]