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# Smallness—the source of innovation

Projects for creating new materials and new functions for advancing nanoelectronics

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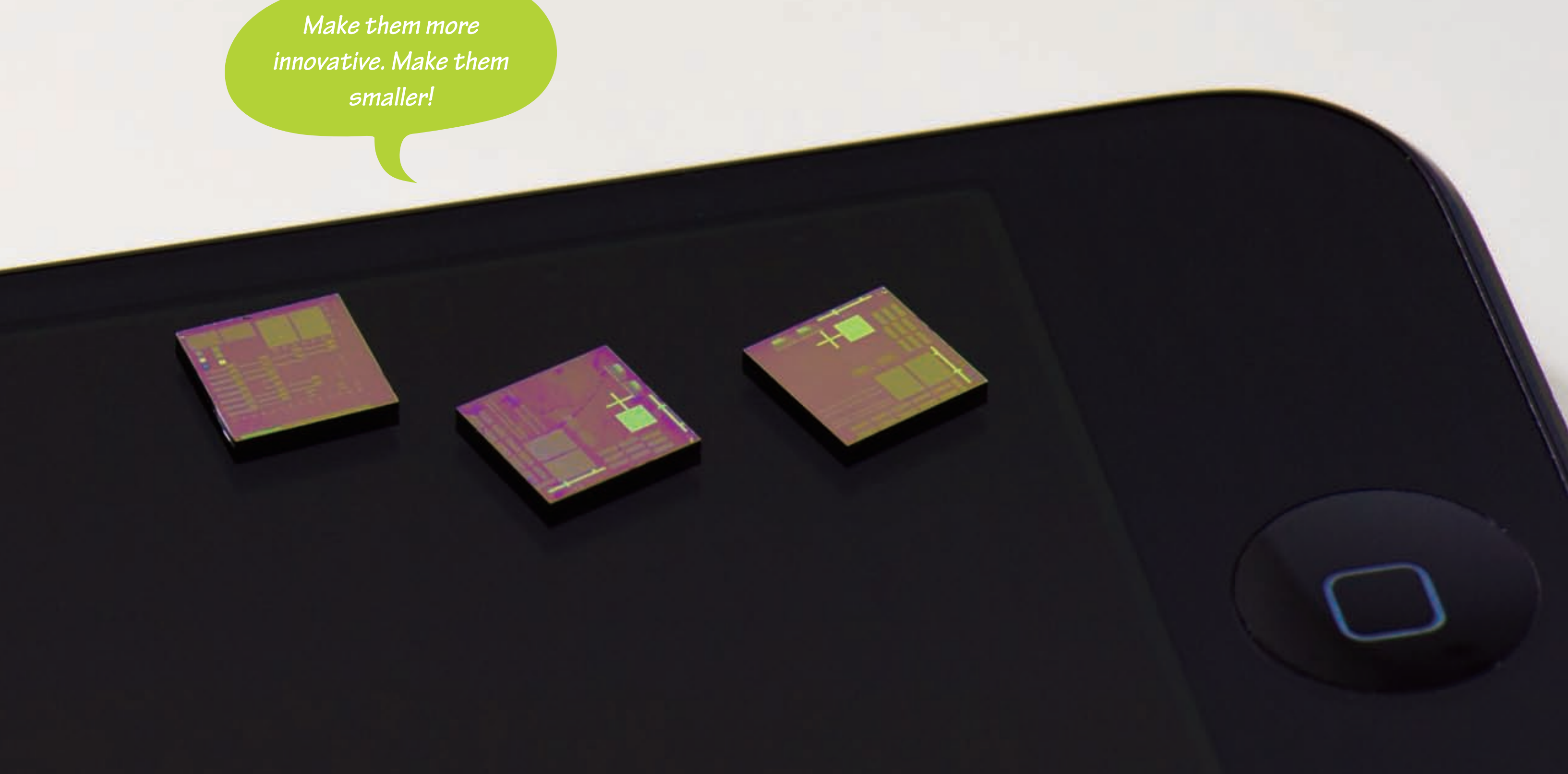
Projects for creating new materials and new functions for advancing nanoelectronics

A roomful of transistors—that’s how it all began.
There was one computer for one building. The storage device was tape.
But from a certain point in time, they started to shrink like magic.
They could be placed on a desktop. It was one computer for one team,
and then one for each person.
Storage devices became palm-sized and computing power leaped dramatically.
Computers became thinner and more lightweight.
They began to be carried around in a pocket.
Now, they can be handheld or even wearable as a watch or eyeglasses.

Of course, this was no magic.
The change was caused by the minimization of transistor chips,
known as Moore's law.
Today, about one billion transistors are packed on an around 100 mm$^2$ die.
But what will the future of this evolution be?
The process of trial and error continues.
How can we overcome the number of problems that emerge from the shrinking?
One of the solutions is the materials.

This feature takes a look at how materials can contribute to the frontiers of nanoelectronics from diverse angles.

Make them more innovative. Make them smaller.



# Nano-Electronics for the Future
# Toward Achieving Super-Power-Saving Devices through the Best Mix of Materials, Structure, and System

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**Toyohiro Chikyow**

## The key lies in materials and structure

Looking back at the history of the ICT industry, we have experienced significant changes every decade. Desktop computers which appeared on the scene in the 1990s enabled us to use computers without needing to worry about the electric source or voltage. However, the advent of notebook computers in the 2000s reminded us of the necessity to reduce power consumption, because these devices are powered by batteries as well. Recently, mobile information and communication terminals such as smartphones and tablet computers are coming into the mainstream in the ICT field.

Integrated circuits that support these electronic devices have been improved in functionality through miniaturization and further integration. In addition to these two characteristics, low power consumption has also been desired recently. In particular, further reduction in power consumption is demanded for devices applied in mobile terminal units which are powered by small batteries (Fig. 1). The key to achieve this lies in materials and structure.

## Miniaturization and logic devices

Conventionally, the popular logic device has been bulk MOSFET, which is MOSFET produced on the Si substrate. Now, in response to the demand for low power consumption, the following two methods are being proposed.

One method is called FD-SOI, which stands for Fully-Depleted Silicon-On-Insular. FD-SOI has a structure wherein MOSFET is produced on Silicon-on-Insular (SOI) that is made by sticking a thin single-crystal silicon film onto an insulating film. In this structure, the thin Si film serves as a channel with low impurities. Therefore, FD-SOI shows less short-channel effects, and even when the gate length is shortened, the change in the threshold gate voltage arising due to the impurity concentration is not so large. In addition to these significant characteristics, FD-SOI allows on/off switching even when the gate voltage is reduced to around 0.7V and therefore it is expected to be favorable for miniaturization and low voltage. There are growing expectations for this MOSFET on an SOI to be used as logic devices such as CPUs. Currently, development of FD-SOI is being promoted by a European electronics company, STMicroelectronics, and others, with a prospect for commercialization at a gate length of 20nm or shorter. When further progress is made in miniaturization, it will be necessary to connect higher-k materials directly to the semiconductor. Moreover, a new type of metal gate will be needed to control the work function precisely and an amorphous metal gate will be needed to adapt to miniaturization.

The other method is FinFET (Fig. 2). The basic principle of the FinFET structure is the XMOS structure, which was born in Japan. The XMOS structure enables control of the short-channel effects and reduction of the leak voltage by controlling the voltage at both the upper and lower gates. The FinFET structure can be made by placing the XMOS structure on its side. As in the case of FD-SOI, the "fin" that serves as a channel in the FinFET structure is thin, so this structure has more advantages in miniaturization processing than the current bulk MOSFET, such as that it can control the short-channel effects and prevent dispersion in the threshold voltage arising due to impurities. The FinFET has been adopted for Intel's CPUs and it can be applied at a gate length of 22nm or shorter. The problem is that it is necessary to raise the precision in miniaturization processing in order to produce the fin structure. It is also necessary to control the work function of the gate in order to control the threshold voltage precisely. Moreover, amorphous materials are needed as gate stack materials in order to achieve miniaturization and 3D-structure.

## Memory devices and new materials

At present, memory devices are roughly categorized into two types: DRAM (Dynamic Random Access Memory), which is volatile and operates at a high speed; and NAND flash memory, which requires more time to write and erase data but allows the recording of a vast amount of data in a non-volatile form. As an emerging memory device, ReRAM (resistive random access memory) is attracting attention as a possible substitute for

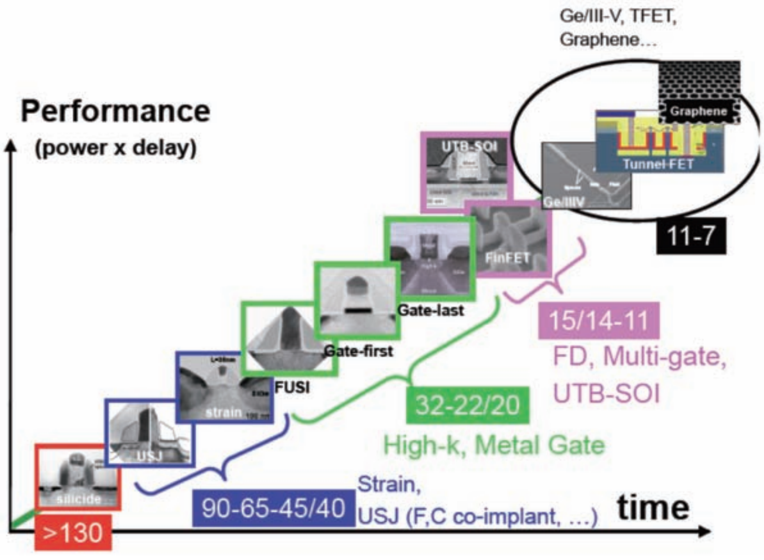

**Fig. 1** Trends in miniaturization of MOSFET. FD-SOI and FinFET will come into the mainstream in the future.(from the presentation at INC7 by Dr. Paul Heremans and his collaborators)

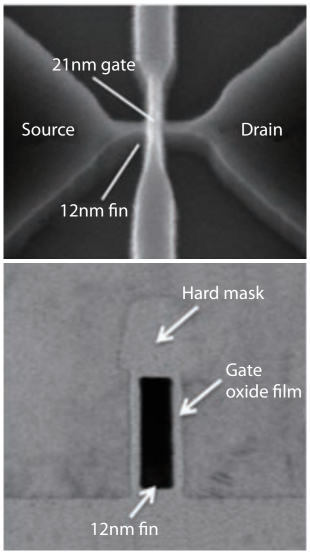

**Fig. 2** Pictures of FinFET (Provided by Dr. Meishoku Masahara, AIST)

NAND flash memory.

### 1) DRAM

DRAM records data by storing electric charges in its capacitors. That is, it requires a certain quantity of electric charge. Along with the advancement in miniaturization of memory devices, the space in which electric charge can be stored has become smaller. This may be one factor that has led to the development of the trench-type capacitor, in which trenches are created so that electric charge can be stored on their side walls in order to secure more space. However, this technology has reached its limit as the aspect ratio—the ratio between the diameter and the depth of the trench hole—has exceeded 1:50.

The future trend is expected to go back to the basic capacitor structure, making DRAM by inserting very high-dielectric materials between parallel electrodes. The materials to be used are required to have a dielectric constant of 200 or higher, which cannot be achieved by the currently available ordinary higher-k materials. Thus, there is a call for new materials that have a very high dielectric constant and low leak current.

### 2) NAND flash memory

NAND flash memory is a non-volatile memory device that is currently most popular. Although it has the capacity to store as much data as 128Gb, as miniaturization advances, we are facing a significant challenge in how to secure the reliability of the gate insulating film that electrons pass through. Furthermore, lowering the writing voltage is also important from the perspective of both securing reliability and reducing power consumption. Through collaboration with the National Institute of Advanced Industrial Science and Technology (AIST), Renesas Electronics Corporation and other parties, NIMS has attempted and succeeded in the development of an insulating film with low writing voltage and high reliability and the realization of a fin-type flash memory.

### 3) ReRAM

ReRAM (resistive random access memory) is now attracting the most attention as a next-generation non-volatile memory. In its structure, oxide is inserted between metal electrodes so that electrons can pass through an aggregation of oxygen vacancies that are created in oxide when supplied with voltage (Fig. 3). In order to create such an aggregation of oxygen vacancies stably, it is essential to understand nano-scale phenomena, such as the control of the valence of oxide and the oxidation-reduction of the metal-oxide interface under the applied voltage. Analysis of these phenomena cannot be made without measuring the state of chemical bonding under the conditions where voltage is applied.

## 3D-structured devices

Attempts are also being made toward laminating individual logic devices or memory devices in a 3D-structure and integrating functions so that calculation and recording can be processed by a single chip. In this attempt, it is necessary to connect the upper device through to the lower device by a wire. This can be achieved by a technology called Through-Silicon-Via (TSV), wherein a fine hole is digged in the silicon substrate in a manner that the hole pierces through the substrate, its periphery is insulated, and it is filled with metal wiring by which electric signals are transmitted (Fig. 4). While this is presently being attempted by creating a hole via plasma etching, or by Cu wiring by plating, a technology for creating a piercing hole more easily and precisely and filling it with wiring materials will be necessary in the future. In particular, conductive materials to be used to fill in the hole will be important. In this field as well, NIMS has attempted and succeeded in the development of highly conductive materials that can form nano-particles and conductive polymer simultaneously.

## Nano-Electronics for the future

Electronics, as a foundation of society, will continue to evolve in the future while introducing new structures supported by the development of new materials. NIMS will further strive to contribute to the advancement of this field.

1) T. Nabatame, M. Kimura, H. Yamada, A. Ohi, T. Ohishi, and T. Chikyow, "Influence of oxygen transfer in Hf-based high-k dielectrics on flatband voltage shift",Thin Solid Films, 520 (2011) 3387–3391.
2) T. Nagata, M. Haemori, Y. Yamashita, H. Yoshikawa, Y. Iwashita, K. Kobayashi, and T. Chikyow, "Bias application hard x-ray photoelectron spectroscopy study of forming process of Cu/HfO2/Pt resistive random access memory structure", Appl. Phys. Lett. 99, (2011) 223517.
3) J. Kawakita and T. Chikyow, "Fast Formation of Conductive Material by Simultaneous Chemical Process for Infilling Through-Silicon Via" ,Jpn. J. Appl. Phys. 51 (2012) 06FG11.

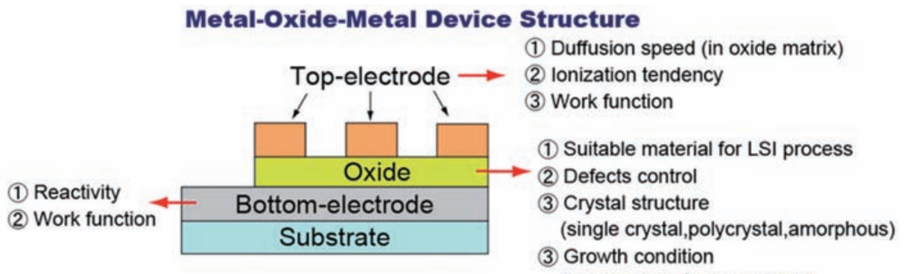

**Fig. 3** Structure of ReRAM, and characteristics of the desired materials

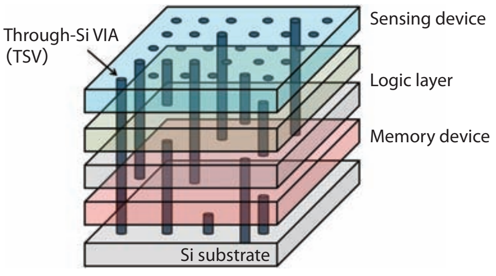

**Fig. 4** Conceptual illustration of a laminated device using TSV

## Profile

**Toyohiro Chikyow** Ph.D (Engineering) Principal Investigator (PI), Nano-Electronic Materials Unit, International Center of Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS). Professor at the Waseda University-NIMS Joint Graduate Program. Visiting professor at the University of Washington, Materials Science and Engineering. Specializes in semiconductor materials and electronic materials. While promoting the development of electronic materials by combinatorial approaches, he is pursing partnerships with private corporations, higher educational institutions and research institutes, at home and abroad. Graduated at Waseda University, Graduate School of Science and Engineering, Department of Electrical Engineering in 1989.

# Optical Surface Analysis and Its Application to Designing Nano-Electronics Materials

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## Semiconductor materials and band diagram

Electronic appliances that we use in everyday life are composed of a variety of semiconductor materials. A semiconductor is a material which has an energy gap (band gap) between the valence band filled with electrons and the conduction band containing vacant seats to accommodate electrons. Semiconductors are characterized by the size of the band gap between the valence band and the conduction band.

In order to produce a device with diverse functions, it is necessary to combine semiconductor materials that have different band gaps. In this process, it is necessary to adjust and equalize to the greatest possible extent the energy levels of the valence bands and conduction bands that electrons and holes move through in order to save power consumption and increase efficiency.

For this purpose, in addition to the band gap, we need information on the positions away from the reference level of the valence band and the conduction band. A band diagram is a diagram that indicates these positions. Among the various options for the reference level, applicable depending on the semiconductor material region being used, we selected the vacuum level, which is a general one. The energy between the vacuum level and the conduction band level is called the electron affinity, and the energy between the vacuum level and the valence band level is called the ionization potential.

## Band diagram measurement system

We overcame the problem with the conventional method of measuring a band diagram, which required multiple measurements, and developed a new system that enables the measurement of a band diagram using a single system and in a single operation, irrespective of the measurement environment (in a vacuum or atmospheric conditions).1), 2) This system allows us to excite electrons at the valence band level to the vacuum level as a result of the photoelectric effect by irradiating them with ultraviolet rays. We can obtain the ionization potential by measuring these electrons with an ammeter incorporated into the system that can measure very small electric currents. At the same time, when reflected or transmitted light is measured by this system, it is absorbed at a certain energy level, which represents a band gap. Thus, we can obtain a band diagram based on information on the valence band and the band gap.

## Importance of band diagram measurement

A band diagram is an important indicator in device designing. We thus far separately measured materials such as organic EL materials and oxide materials. In the future, the combination of the newly developed band diagram measurement system and the combinatorial system (a system that forms sample films of different compositions automatically) will enable us to produce a band diagram library automatically and systematically, driving forward material development at a high speed. Band diagram measurement will also be an effective approach to further the Material Genome Initiative discussed in the report titled "The Competitiveness and Innovative Capacity of the United States,"3) in which the idea of gene analysis is applied to materials science.

1) NIMS Press Release 2012.08.27 http://www.nims.go.jp/eng/news/press/2012/08/p201208270.html
2) Shinjiro Yagyu, Michiko Yoshitake, Masahiro Goto and Toyohiro Chikyow J. Vac. Soc. Jpn.Vol. 56, No. 4, 125-128 2013.
3) The Competitiveness and Innovative Capacity of the United States, January 2012; Department of Commerce Press Release, January 6, 2012; SSTI Weekly Digest, January 11, 2012.

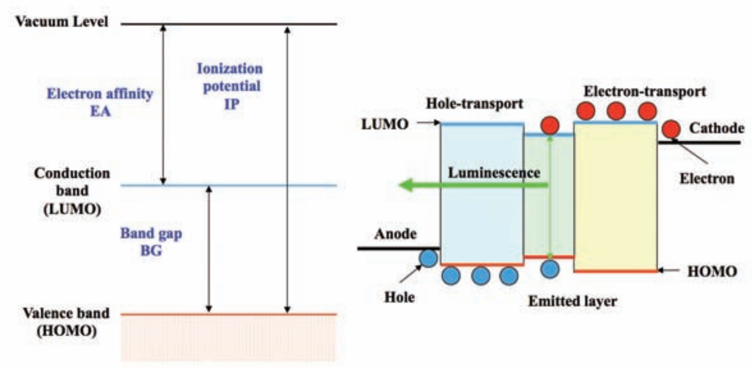

**Fig. 1**
(Upper left) Simplified band diagram
(Upper right) Principle of Operation of OELD

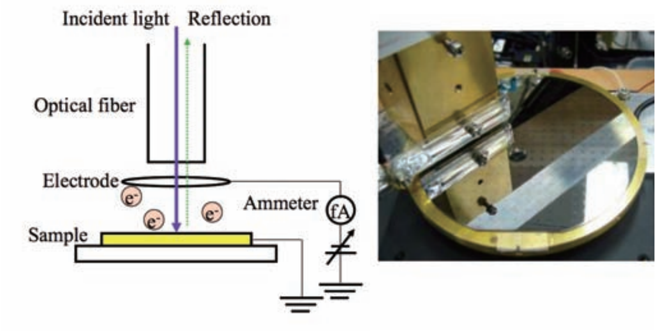

**Fig. 2**
(Upper left) Outline of the band diagram measurement device
(Upper right) Measurement of a combinatorial sample formed on an Si substrate

## Profile

**Shinjiro Yagyu** Ph.D (Engineering) Completed the doctoral course at the University of Tsukuba, Graduate School of Engineering in 2001, and joined NIMS in the same year. He has been a NIMS Senior Researcher since 2005. / **Michiko Yoshitake** Ph.D (Engineering) Joined the National Research Institute for Metals (NRIM) (current NIMS) in 1987. Obtained a Ph.D for her thesis at the University of Tokyo, Graduate School of Engineering in 1992. She has been a NIMS Chief Researcher since 2004, and has held the position of adjunct professor at Charles University in Prague, the Czech Republic, from 2010 to 2013.

# Are Photoisomerizable Molecules Applicable to Electronic Devices?

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## Advantage and Problem of Photoisomerizable Molecules

Because of their diverse functions, organic molecules have been expected to become a major material for electronic devices in the future. However, they will only be valuable assets if their functions are brought out into practical device structures.

A typical example that represents this problem is photoisomerizable molecules. Photoisomerization is a phenomenon in which reversible structural changes occur to a molecule when it is irradiated with visible light and ultraviolet light in turn. These structural changes invoke changes in the properties of the molecule, such as its π-electron conjugated system, energy level, and optical absorption spectrum. To date, application of these characteristics to memory and sensors has been proposed.

We have been studying how we can make use of this advantage of photoisomerizable molecules to produce effective photoelectric conversion devices or memory devices, and reached an idea of applying it to organic transistors.

## Application to organic transistors (1): Photoinduced semiconductor-insulator transition

Figure 1 shows the structure and device characteristics of an organic transistor in which diarylethene molecules form the channel layer, and the light-activated switching operation of the transistor.

By applying an electric current directly to diarylethene molecules, we succeeded in increasing the on/off ratio of the light-activated switch by two orders of magnitude as compared to a similar conventional device. This operation was made possible for the first time in the world by attaching two phenyl groups to each end of the backbone of the diarylethene molecule. We thus developed a new material equipped with the properties of both a photoisomer and a semiconductor by way of an appropriate molecular design.

In the above process, we took advantage of the mechanism wherein the π-electron conjugated system changes significantly along with photoisomerization. In other words, we induced a new phenomenon that could be called "reversible semiconductor-insulator transition" through photoirradiation and applied it to transistor control.[1] We conducted this research jointly with Professor Kenji Matsuda and Assistant Professor Kenji Higashiguchi from Kyoto University.

## Application to organic transistors (2): Multilevel switching with the optical memory function

Some photoisomerizable molecules transform into ion-polarized molecules as a result of photoirradiation. One such example is spiropyran molecules, shown in Figure 2 (a).

We had an idea that we might be able to control the flow of electric charge using this ion-polarized molecule, and based on this idea, we produced an organic transistor by doping spiropyran molecules to the semiconductor polymer (PTAA). As a result, we achieved an optical-controlled organic transistor in which ion-polarized spiropyran molecules function as an electric charge scatterer.[2]

We developed this device operation further and produced a dual-gate transistor consisting of a layer doped with spiropyran molecules and an undoped layer (Fig. 2(b)), which enabled the operation of a multilevel switching device that can control the electric current using a optical gate and two voltage gates, as shown in Figure 2 (c). This device is not only capable of controlling the electric current by voltage but is also equipped with a photo-memory function.

1) R. Hayakawa, K. Higashiguchi, K. Matsuda, T. Chikyow, Y. Wakayama, ACS Appl. Mater.& Interface 5 (2013) 3625.
2) Y. Ishiguro, R. Hayakawa, T. Chikyow , Y. Wakayama J. Mater. Chem. C 1 (2013) 3012.

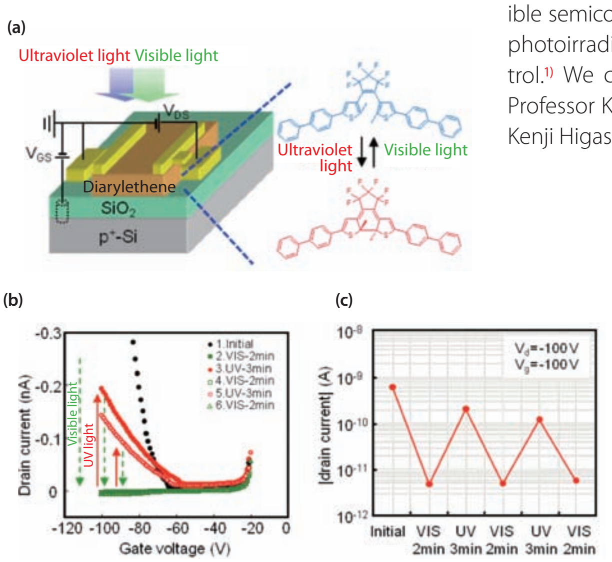

**Fig. 1** **(a)** Transistor device in which diarylethene molecules form the channel layer; molecular structure and open-circular/closed-circular photoisomerization
**(b)** Transistor characteristics and optical control
**(c)** Reversible optical control of drain current

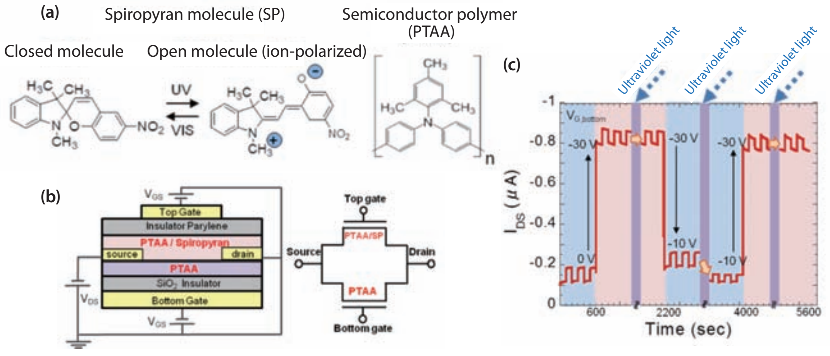

**Fig. 2** **(a)** Photoisomerization of spiropyran molecules and semiconductor polymer (PTAA)
**(b)** Dual-gate transistor structure in which the layer doped with spiropyran molecules and the undoped layer are stacked
**(c)** Multilevel switching operation with the memory function, controlled by the top gate, bottom gate, and light gate

## Profile

**Yutaka Wakayama** Ph.D (Engineering) Completed a doctoral course at the University of Tsukuba, Graduate School. After working for Asahi Glass Co., Ltd., JST-ERATO, and Max-Planck-Institut für Mikrostrukturphysik, he joined the National Research Institute for Metals (NRIM; currently NIMS) in 1999. He concurrently holds the position of faculty member of the Kyushu-NIMS Graduate Program. **/**
**Ryoma Hayakawa** Ph.D (Engineering) Completed a doctoral course at Osaka Prefectural University Graduate School. Prior to assuming the current position in July 2012, he was a member of JSPS-PD in 2006, a NIMS Postdoctoral Researcher in 2008, and an ICYS-MANA Researcher in 2010.

# Material Designing of Metal Gate Electrodes to Control the Threshold Voltage

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## What is required for Metal Gate Electrodes?

For a complementary metal-oxide-semiconductor (CMOS), which has a gate stack structure comprised of "metal gate electrode – high dielectric gate insulator (High-k) – semiconductor," the threshold voltage (Vth) is required to be controlled. Several methods have been proposed to control the Vth, and changing the work function of metal gate electrode materials is one such method.

Metal gate electrode materials of n-type metal-oxide-semiconductor field-effect transistors (nMOSFET), through which electrons are transported, and of p-type metal-oxide-semiconductor field-effect transistors (pMOSFET), through which holes are transported, must have a work function close to the conduction-band edge of silicon (4.05eV; nMOSFET) or to the valence-band edge (5.17eV; pMOSFET), respectively. Therefore, with regard to silicon technology node 22nm-generation CMOS, TiN/Al is considered as candidate metal gate electrode material for nMOSFET, and TiN is considered as such for pMOSFET.

The work function of TiN is about 4.6~4.8eV. In the case of nMOSFET, Al atoms with a low work function, 4.06eV, diffuse to TiN at the processing temperature, thereby making the work function of the metal gate electrode close to around 4eV.

## Approach in NIMS

We systematically investigated how TaC (tantalum carbide) materials work as metal gate electrode materials when atoms with a low work function such as Al atoms (4.06eV) and Y atoms (3.1eV) are introduced to them (Fig. 1). As the amount of Al atoms or Y atoms increased, the flat band voltage changed in the negative direction. This may be caused by a decrease in the work function of the TaC materials. Thus, by introducing atoms with a low work function, we can design metal gate electrode materials with a low work function, which are required for nMOSFET.

As for the production of pMOSFET, we have been attempting another approach in addition to designing metal gate electrode materials with a high work function.

This approach focuses on the changes in the flat band voltage using the formation of an electric double layer (dipole) on the High-k/$SiO_2$ hetero-interface. These changes can be explained based on the mechanism in which, when a High-k film is put onto an $SiO_2$ film, the oxygen on the interface moves toward stabilizing the structure, and charge transfer takes place accordingly.

Figure 2 shows the changes of the flat band voltage in the positive direction along with the changes in the annealing temperature of a TaC metal gate electrode to which Al atoms are introduced. This suggests that as the annealing temperature increased, Al atoms began to diffuse from the TaC metal gate electrode to the High-k layer, and finally reached the $SiO_2$ interlayer and formed a dipole.

The understanding of the effect of a dipole and the technique to adjust the work function of a metal gate electrode as explained above are expected to greatly help in showing a direction for the designing of metal gate electrode materials in the process of producing a FinFET with a 3D structure or CMOS with a gate-all-around (GAA) structure using nanotube channels.

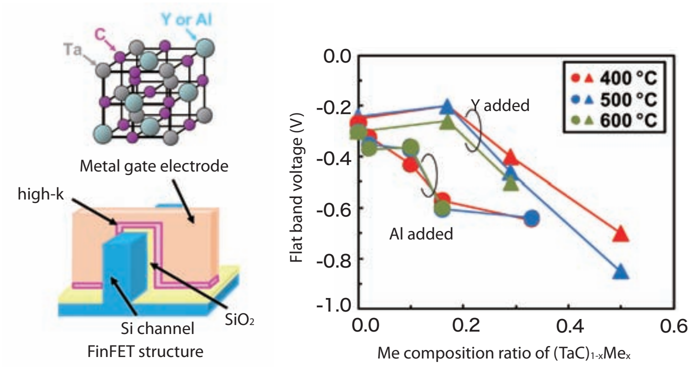

**Fig. 1**
FinFET structure of the metal gate electrode/High-k film, and the changes in the negative direction of the flat band voltage of the TaC metal gate electrode to which Al atoms or Y atoms are introduced

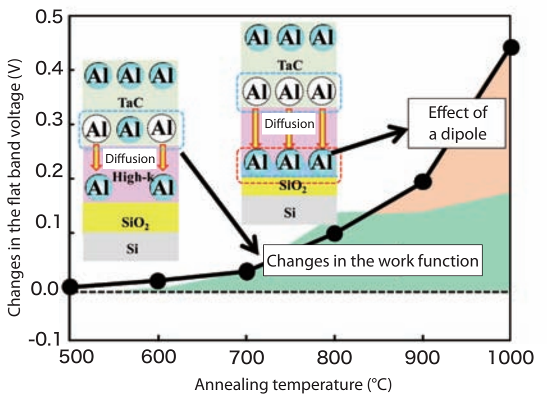

**Fig. 2**
Changes in the work function of the TaC metal gate electrode, and the changes in the positive direction of the flat band voltage along with the formation of a dipole on the AlOx/$SiO_2$ interface

## Profile

**Toshihide Nabatame** Ph.D (Engineering) Completed a master's course at Tohoku University Graduate School. Joined Hitachi Research Laboratory, Hitachi, Ltd. as a senior researcher in 1987. Obtained a Ph.D at Tokyo Institute of Technology in 1994. Worked for Renesas Technology Corporation from 2003 to 2009. He has held the present position since 2009. He has also held the position of visiting professor at Shibaura Institute of Technology since 2011 and at Meiji University since 2012.

# Low-Voltage SEM Opening a Future Path for Observation of Materials

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National Institute of Advanced Industrial Science and Technology (AIST)
**Kazuhiro Kumagai**

## A World Observed by 100-V EM

As a means to observe the surface vicinity of materials, we have been engaged in the development of an scanning electron microscope (SEM) opertating with electrons at 100V. The depth of electron penetration decreases roughly as the inverse square of the electron energy. As an electron accelerated at 100V penetrates only about 10nm into materials , we can obtain information on the vicinity of the surface of the materials by detecting the secondary electron signals emitted by this electron injection.

We aim to develop the method to observe a nanostructure which is, for example, embedded in the top surface, in a non-destructive and three-dimensional manner. Ordinary types of SEM do not allow repeated observations because the surface becomes contaminated after only one observation. To overcome this problem, we have developed a new device the whole of which is in ultra-high vacuum (see the picture of the cover page).

Figure 1 indicates the secondary electron images of $Si_3N_4$ ribbons shot at different incident electron energies. The ribbon marked with an arrow which is seen above the others at 100V appears to be beneath the others at 3kV. Thus, secondary electron images show us a mysterious world. Progress in the study of electron-matter interaction has revealed that the paradox presented in Figure 1 can be resolved by analyzing the process of secondary electron emission quantitatively.[1)]

Figure 2 represents the dependence on the incident electron energy of the secondary electron emission yield from $Si_3N_4$ ribbons. It shows that when accelerated voltage is changed, the proportion of secondary electrons emitted from each ribbon varies, and in some cases, the signals from the ribbon which is beneath the others are intensified, creating an illusion that the ribbon is above the others.

## Obtaining more useful information through spectroscopy of electrons emitted from a specimen

We initially thought that this ultra-low-voltage EM would be a key to open a new world for nanoscience. However, as we proceeded with our research, we found that we would be able to obtain more useful information through spectroscopy of electrons emitted from a specimen.

For example, we can erase a nanosheet covering the surface of the materials from an image or make it appear in the image.[2)] We can also analyze the curvature of the energy band on the surface of the semiconductor based on the image contrast.[3)]

At present, we are tackling challenges such as visualizing defects that cause leakage of a high-k insulating film, which is a component of next-generation semiconductors, and making the functioning of resistive random access memory (ReRAM) viewable. If we are able to detect defects causing a failure in a semiconductor before the failure appears, that would be revolutionary progress in the context of reliability assessment.

Secondary electrons contain information on diverse interactions that the accelerated electrons receive after their incidence to the specimen. Research on secondary electrons has sometimes been described as equivalent to searching for treasures in a trash can. However, we have been making efforts to take a step forward in this field, by taking advantage of low-voltage electrons and spectroscopic detection of energy.

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2) K. Kumagai, T. Sekiguchi, K. Fukuda and T. Sasaki, Appl. Phys. Express. 2, 105504 (2009)
3) K. Kumagai, and T. Sekiguchi, Phys. Stat. Solidi C 8, 1293 (2011)

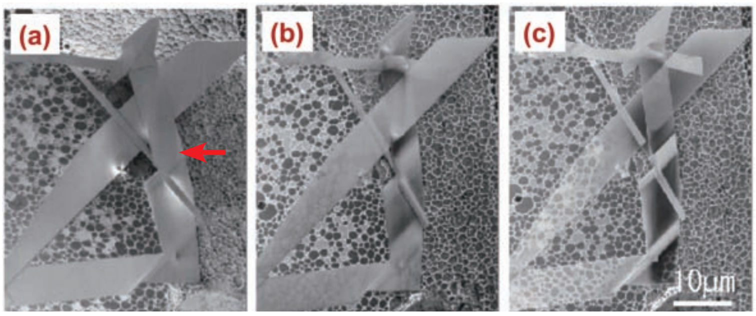
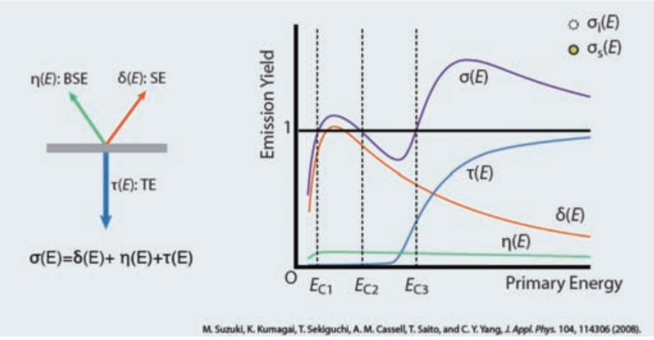


**Fig. 1**
Paradox of overlapping secondary electron images of $Si_3N_4$ ribbons
Accelerated voltage: **(a)** 100V, **(b)** 3 kV, **(c)** 5 kV



M. Suzuki, K. Kumagai, T. Sekiguchi, A. M. Cassell, T. Saito, and C. Y. Yang, *J. Appl. Phys.* 104, 114306 (2008).

**Fig. 2**
Dependence on the incident electron energy of the secondary electron emission yield from $Si_3N_4$ ribbons
σ: total emission, δ: secondary electrons; η: reflection electrons; τ: transmission electrons

Profile

**Takashi Sekiguchi** Ph.D (Science) Prior to assuming the current position, he worked as an assistant and an assistant professor at the Institute for Materials Research, Tohoku University, and as a Senior Researcher at the National Research Institute for Metals (NRIM). He concurrently holds the position of professor at the University of Tsukuba. He specializes in researching lattice defects in semiconductors. **/ Kazuhiro Kumagai** Ph.D (Engineering) Completed the Doctoral Program in Materials and Science and Engineering at the University of Tsukuba, Graduate School of Pure and Applied Sciences. He currently holds a position in the National Metrology Institute of Japan, the National Institute of Advanced Industrial Science and Technology (AIST).

# Development of Materials of Valence-Controlled Oxide Resistance-Change Memory by Combinatorial Approach

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## Achieving ReRAM using $HfO_2$ as gate materials

An explosive increase in the amount of information, as exemplified by the sharing of diverse electronic data recently referred to with the keyword “big data,” and the expansion of cloud computing services used on a personal level, is creating demand for a memory device that enables high-density storage and processing of information at low power consumption and at a high speed.

Instead of applying different types of memory devices such as high-speed DRAM and high-capacity and non-volatile flash memory depending on the intended use, as has been conventionally conducted, efforts are being made toward the development of “universal memory,” which covers all characteristics desired of memory devices, namely, high-integration, high-speed operation, non-volatility, and low power consumption. Candidates for this type of memory include resistance-change RAM (ReRAM), phase-change RAM (PRAM), and magnetoresistive RAM (MRAM), among which ReRAM has attracted attention for its simple “metal-oxide-metal” structure and suitability for miniaturization. However, there is a mountainous pile of problems yet to be solved in terms of securing reliability and controlling variations in characteristics. Success in solving these problems depends on the choice of electrode materials and oxide materials.

From this viewpoint, we tackled and succeeded in the development of ReRAM using $HfO_2$, which is a currently available high-dielectric material, as gate materials. Furthermore, by combining various types of electrode materials, we clarified the changes in interface reactions on the metal-oxide interface as well as the migrations of atoms and vacancies upon application of an electric field, and thereby revealed that there is a close relationship between the process of forming the low-resistance layer and oxygen vacancy in the oxide.[1), 2)]

Based on these findings, we combined the leakage current characteristics at Power OFF, which are suitable for ReRAM, with an oxide whose valence fluctuates as a method of controlling the switching voltage, in an attempt to make the valence fluctuate intentionally and compensate for the oxygen vacancy, thereby controlling the switching characteristics of ReRAM.[3)]

## Aiming to develop ReRAM devices

In this attempt, among candidates for high-k materials, we used Ta-oxide and Nb-oxide, which are similar in their physical properties such as ion radius but which have multiple valences and different energy levels for oxidization. In the preparation and characterization of a specimen, we applied the binary composition-based combinatorial approach[Note 1] (Fig. 1). Figure 2 shows the results of mapping of metal elements measured by X-ray photoelectron spectroscopy (XPS).

According to the mapping results, the shift of Ta4f to the lower energy side that occurred when Nb was added to Ta (indicated by Arrow A in Fig. 2 (a)), coupled with the oxygen’s energy shifts and intensity changes, signifies the formation of an oxygen vacancy. On the other hand, Nb3d also shifted to the lower energy side when Ta was added to Nb (indicated by Arrow B in Fig. 2 (a)), but the mapping results suggest that the oxygen vacancy caused by the valence fluctuation was compensated for, coupled with the analyses of oxygen and oxidation energy.

In terms of electrical characteristics, changes in the leakage characteristics and fluctuations in the forming voltage were observed according to the results of XPS mapping. The leakage current was reduced within the range of 0<Ta/Nb<0.5 and a forming voltage of around 1V was achieved (Fig. 2 (b)). These findings indicate that it is possible to control the process wherein the resistance change phenomenon takes place and to improve the leakage characteristics by using the oxide layer as valence-fluctuating materials.

Based on the results described above, we will continue to carry out research on materials designing for securing reliability of ReRAM and controlling variations in its characteristics, with the goal of developing ReRAM devices.

1) M. Haemori, T. Nagata et al. Applied Physics Express, Vol. 2, 061401 (2009)
2) T. Nagata et al. Journal of Materials Research, Vol. 27, 869 (2012)
3) T. Nagata et al. ACS Combinatorial Science, Vol 15, 435 (2013)

Note 1: The combinatorial approach is an approach for rapid search of new materials wherein a multicomponent thin film (composed of two or three components) is produced in a single specimen and characterized as a whole by combining thin film growth achieved by the physical vapor deposition method with a PC-controlled mask of a special shape and a target exchange mechanism.

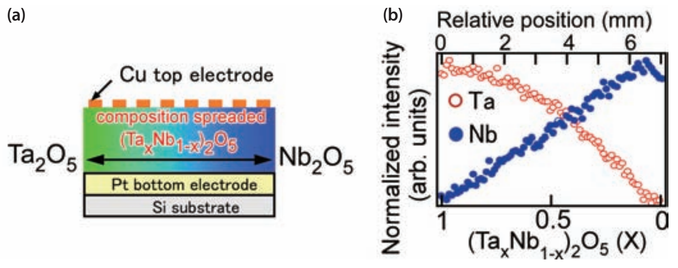

**Fig. 1** **(a)** Conceptual illustration of the specimen produced by the combinatorial approach
**(b)** Results of composition analysis of such specimen by X-ray fluorescence method
It was observed that one specimen was a Ta-composite thin film and the other was an Nb-composite thin film.

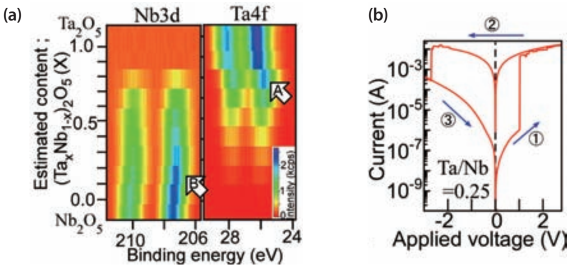

**Fig. 2** **(a)** Results of XPS mapping of the core spectra of Nb3d and Ta4f
**(b)** Voltage-current characteristics for $(Ta_{0.2}Nb_{0.8})_2O_5$
The voltage was swept in the direction of ①-②-③.

## Profile

**Takahiro Nagata** Ph.D (Engineering) Completed a doctoral program at Osaka Prefecture University Graduate School. Prior to assuming the current position, he worked at NIMS as a post-doctoral researcher since 2003 and Researcher since 2006. He also worked as a visiting researcher at the University of California, Santa Barbara, from 2008 to 2009. **/ Toyohiro Chikyow** Please see P. 5 for his profile.

INTERVIEW

# Unless the research results are useful for society, it is only substance research, and not materials research

## Hideo Hosono

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**Professor Hideo Hosono of the Frontier Research Center, Tokyo Institute of Technology (TITECH), won the NIMS Award 2013 for his research achievement titled "Development of New Functionalities Arising from Electrons in Oxide-Based Solids." For many years, Professor Hosono has been providing extensive advice on research at NIMS as a member of the NIMS Advisory Board or as an external advisor.We interviewed him about his ideas in ideal materials research in general and about the ideal research to be conducted in universities and incorporated administrative agencies, respectively.**

**――Congratulations on your receiving the NIMS Award, though it is only natural that you won the award.**

**Hosono(H):** Thank you very much. I am grateful that I was chosen.

**―― Your research covers an extensive range of themes.**

**H:** Well, not as extensive as it seems. In short, I have only studied how to use electrons in solid materials. For example, a solid material becomes a semiconductor if an electric current is generated by applying an electric field to electrons within the material, and becomes a catalyst if the electrons are allowed to react with molecules at the surface of the material. Indeed, it is not easy to find how to use electrons within a solid material, but as I gradually became experienced in such study, I was able to find some useful behaviors according to the material, and I came to understand various things. I have been carrying out such study for 20 years now, but there is always more to learn, as it is quite a deep field to study.

**――What would you like to do in the future?**

**H:** Study catalysts. Many aspects of catalysts are still unknown, and I want to try something unique.

**―― You always mention the importance of students when carrying out such studies.**

**H:** Absolutely. In the case of a university, university minus students equals zero. The presence of students is essential, and the most important product is the students. It should not take the form of mere education at a graduate school where the teacher teaches students in a one-way direction. Rather, the teacher and the students should keep an adult-adult relationship.

In fact, there are so many things we can learn from students. It usually is the case that smarter students do not follow teachers' instructions, and they try to test teachers' abilities. In the old days, there were many teachers who acted arrogantly within Japan, but became quiet when they were abroad. However, that doesn't pass any longer in cutting-edge research. Teachers must always keep the same attitude, everywhere. So, I believe that a strict relationship with some tension is indispensable between teachers and students with regard to research.

**―― I think university research is basically oriented toward creating seed technology, but you emphasize that research results need to be useful for society.**

**H:** Unless we are strongly conscious of achieving results that are useful for society, it is only substance research, and not materials research. There is a term "next-generation materials." Frankly speaking, next-generation materials are materials that are not useful immediately. That may be fine for young researchers, but when you become my age, it is not satisfying to only pursue next-generation materials. Before we retire, we want to achieve even just one groundbreaking result. I think the way in which we can fulfill our responsibilities is to make practical materials and contribute to society. In that sense, cooperation with private companies is important. One thing that concerns me is that universities are too inclined to pursue next-generation materials, and companies are too inclined to overemphasize that they have created a technology, even if it is clearly based on the research results of universities. That can damage the trust relationship between them. I believe the value of materials development is determined by how much the materials meet the social needs.

**―― Lastly, do you have any requests concerning research at NIMS?**

**H:** For universities, students are essential, but for NIMS, original research that is neither conducted by universities nor companies is considered to be the most important. Then, whether or not the results of such research can be transferred to industry will come into question. Since universities' top priority is to secure academic originality, they compete against others to publish their research findings, in principle. In contrast, NIMS can have closed relationship with companies. I think NIMS should fully leverage such advantages. N

**Hideo Hosono** Doctor of Engineering. Graduated from Tokyo Metropolitan University, and completed a doctoral course at a Graduate School of the same university. After working for the Nagoya Institute of Technology, the National Institute for Molecular Science, and Tokyo Institute of Technology (Associate Professor), became Professor at Tokyo Institute of Technology in 1999 (Materials and Structures Laboratory). 1999–2004 Research director of "HOSONO Transparent ElectroActive Materials" at JST ERATO, 2002–2007 Program leader of Tokyo Institute of Technology "Nanomaterial Frontier Cultivation for Industrial Collaboration" under MEXT 21st Century COE Program, 2004–2010 Project leader of JST ERATO-SORST "Transparent Functional Oxide Project." Currently, core researcher of the FIRST Program.

# NIMS NEWS

## 1 NIMS Signed Comprehensive Collaborative Agreement with Nepal Academy of Science and Technology

On August 1st, Vice Chancellor of Nepal Academy of Science and Technology (NAST), Professor Surendra Raj Kafle paid a visit to NIMS and concluded a Comprehensive Collaborative Agreement (a sister institute agreement) in the presence of H. E. Dr. & Mrs. Madan Kumar Bhattarai, Nepalese Ambassador Extraordinary and Plenipotentiary to Japan.

NAST was established to take responsibility for development and promotion of science and technology in 1982 consisting of 24 academicians and 150 employee at present. NAST itself is a research institution and also it supports academic activities in Nepal by providing a scholarship and research funds, implementing collaboration and academic evaluation, advising on governmental policy, assisting foundation of research institutions both financially and technically.

Interaction between NIMS and NAST started by a visit of the president of the Nepal Chemical Society (a professor of Tribhuvan University) in 2010 and NIMS has received 6 Nepalese researchers so far.

With this agreement, the interaction between the two institutions, such as student and post-doc dispatch, is expected to be enhanced.

(left) President Ushioda (center) Ambassador and Mrs. Bhattarai (right) VC Prof. Kafle.

## 2 The impact factor of STAM keeps growing

Science and Technology of Advanced Materials (STAM) is published by NIMS in partnership with IOP Publishing. STAM is an international, peer-reviewed, open access journal with all articles accessible free of charge at http://iopscience.iop.org/stam/. The journal covers a wide variety of materials science research fields including biomaterials, green technology and nanodevices. Its Editorial Boards represent 10 countries and are headed by the NIMS Fellow Toyonobu Yoshida.

According to Thomson Reuters, STAM ranks 35th out of 239 journals worldwide in the category of Materials Science & Multidisciplinary; it is the leading materials science journal published in Japan. STAM welcomes high-quality articles, proposals for potential Focus Issues, and any suggestions for improvement, which can be submitted via the links below.

http://www.editorialmanager.com/stam/

STAM's Impact Factor Trends (Thomson Reuters, 2012).

# Hello from NIMS

**Dear NIMS NOW readers,**

When we decided to move to Japan, we knew it was going to be a completely unique experience. Then it was time to apply for an ICYS position, which I successfully received, and the dream started. We, Zaira (my wife) and I, left our lives and beloved family and friends in Barcelona to live a very special time in this exotic country.

At the "Tsukuba Ranch," as a close friend used to call this city, there are many small things to enjoy, such as hearing the frogs on a hot summer night from our apartment's balcony and seeing the rice fields dancing under the sun.

Besides these experiences, my daily working life in NIMS is quite motivating, for two main reasons: the high level facilities that are available, and having the chance to collaborate and discuss with other colleagues. We feel so grateful to have met so many people, and it's great to share this time with its many unforgettable moments.

**Cesar MORENO SIERRA** (Spain)
February 1, 2012-Present
ICYS

Disguised as a samurai warrior.

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cover image:UHV(Ultra-High Vacuum) Low Energy Electron Microscope

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