from Tsukuba, Japan to the world

NIMS NOW International

National Institute for Materials Science

Vol.2 No.10 August, 2004

SPECIAL FEATURES

Frontline of Analysis and Evaluation

Expansion of Submicron Region Analysis by Electron Micro-Analyzer

Takashi Kimura
Surface Analysis Group
Materials Analysis Station (MAS)

The electron probe microanalyzer (EPMA) is a device which is used to investigate the types and concentrations of elements included in samples by causing a narrowly focused electron beam to collide with the sample and detecting the X-rays generated at that time. It is the most generally used analytical device in the field of materials science and is actively employed around the world. Unfortunately, because the electrons which collide with the sample expand upon entering the sample interior, the minimum size which can be analyzed expands to the micron (μm) order, and analysis of the submicron region, which is required in recent new materials development, had been difficult. We therefore developed the world's first new-type FE-EPMA (**Fig. 1**), which is equipped with a field emission (FE) electron gun. As features, the beam diameter does not increase even at low electron acceleration energies (acceleration voltage) and furthermore, a large current can be applied.

The characteristics of the device were investigated in order to maximize its performance. **Fig. 2** shows the results of a measurement of the minimum size which can be analyzed at various acceleration voltages and beam currents. These are the results of an analysis of the boundary between copper (Cu) and nickel (Ni). With the new FE-EPMA, the analysis size is smaller than with the tungsten (W) filament-mounted EPMA in all current ranges, and there are no large changes in the analysis size when the current is varied (20 kV). This means that, at the same spatial resolution, analysis can be completed in a shorter time because the analysis can be performed with a larger current value than with W.

The series of photos (**Fig. 3**) are the results of observation of the distribution of compounds of nickel (Ni) and silicon (Si) precipitated in pure copper (Cu). This analysis was performed at an acceleration voltage of 10 kV and beam current of 30 nA. The time required for analysis was approximately 1.8 hours, and the analysis was completed in 1/4 of the conventional time. The distribution of compounds with sizes of less than 100 nm could be clearly observed in the analysis results. We are continuing to develop innovations which will further improve spatial resolution.

Fig. 1: New-type FE-EPMA with FE electron gun.

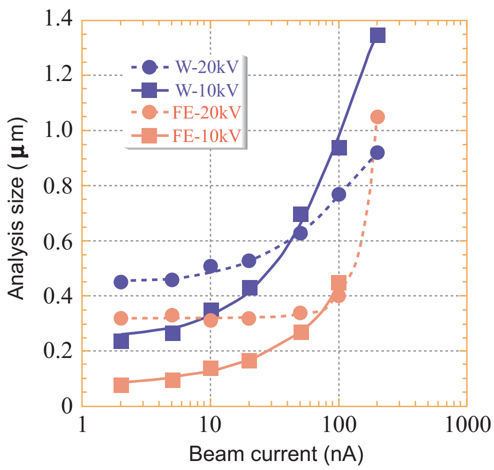


Fig. 2: Relationship of beam current and analysis size.

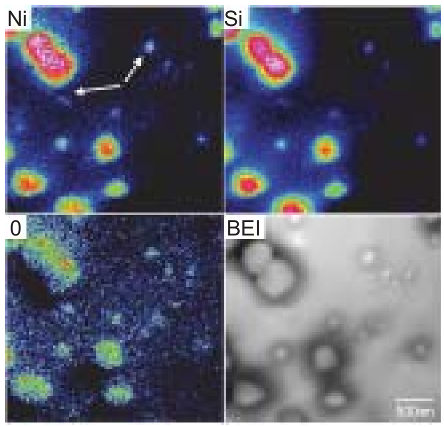


Fig. 3: Results of observation of Ni-Si compounds precipitated in Cu. (BEI: Backscattered Electron Image)

In this issue

Frontline of Analysis and Evaluation

SPECIAL FEATURES

Development of High-Accuracy Evaluation Method for Electron Beam Irradiation Damage

Shigeo Tanuma
Surface Analysis Group
Materials Analysis Station (MAS)

In recent years, with progressively higher integration of semiconductor elements and other devices, characterization of the surface composition and structure in extremely small regions has become an important challenge. Accompanying this, the surface analysis and observation are performed with the Auger electron spectrometer (AES) and scanning electron microscope (SEM) using an electron beam focused to the nm order. However, this causes substantial damage to the sample surface, including decomposition and chemical reduction of the sample, which has become a serious problem. Until now, there had been no method of quantitative evaluation of damage. Damage has been judged qualitatively from changes in the form of the Auger spectrum or degradation (changes in shape or color) of the sample surface. However, quantitative evaluation of the degradation phenomena which occur at the sample surface as a result of electron beam irradiation is indispensable for accurate material evaluation.

Therefore, the Surface Analysis Group developed a method of quantitative evaluation for the surface damage caused by electron beam irradiation on the surface of a silicon dioxide thin film (SiO_2/Si) using AES. This method detects ultratrace Si metal components formed by the decomposition of the sample surface by the electron beam. The method is currently being proposed for joint international research in a VAMAS project. To confirm the effectiveness of the developed method, the prepared samples are being distributed to 21 research institutes in 3 countries for round-robin tests. (Tests by multiple institutes using a unified analysis procedures, which is an indispensable method for international standardization.)

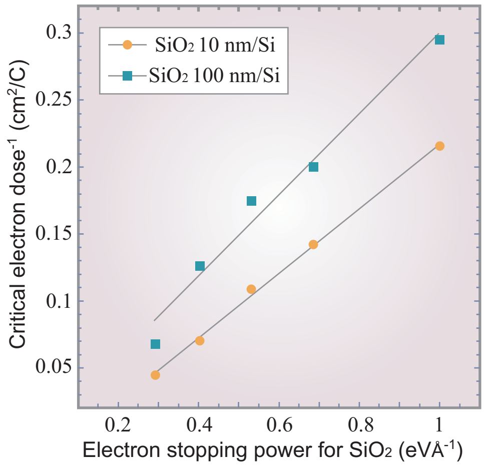


Fig: Relationship between critical electron dose and electron stopping power in electron beam damage of silicon dioxide (SiO_2 (100, 10 nm) /Si) samples.

As shown in the **figure**, we also investigated the relationship between the critical electron dose (minimum electron dose for sample degradation) in the SiO_2 thin film measured by this method and the electron stopping power (energy loss per unit path length of electrons travel through a solid) of the SiO_2 thin film. From this, it was found that the inverse of the critical electron dose in electron beam irradiation damage of the SiO_2 sample surface (i.e., the ease of decomposition of the sample surface) is proportional to the electron stopping power in the 3-15 keV electron accelerating voltage range. It was also found that this tendency does not depend on the SiO_2 film thickness. This means that electron stopping power provides a good index of sample surface damage in the low energy region. Based on this, it is easy to set the conditions for accurate observation and analysis of micro- regions by SEM, AES, or similar techniques while avoiding sample damage.

If the accuracy and practicality of this method are verified in the international round-robin tests currently in progress, it is expected to become an international standard for the evaluation method for sample surface damage due to electron beam irradiation.

For further information, please visit: http://www.nims.go.jp/analysis/e/index_e.html

NIMS NEWS

MOU with National Nano Device Laboratories in Taiwan

On May 31, the NIMS Biomaterials Center (BMC) signed an MOU with the National Nano Device Laboratories (NDL) of Taiwan's National Applied Research Laboratories (NARL). The NDL is one research unit among six belonging to the NARL and has a staff of 150 engaged in research. The two sides plan to promote joint research, conduct mutual exchanges of researchers, and exchange information on research and technical development in fields such as biochip creation, nano fabrication, development of molecular devices using biomaterials, and biomedical engineering.

NIMS Ecomaterials Center Signs MOU with Switzerland's EMPA

On April 5, the Ecomaterials Center (EMC) signed an MOU with the Swiss Federal Laboratories for Materials Testing and Research (EMPA, located in Dubendorf). EMC and EMPA agreed to mutual visits and personnel exchanges by the two sides in order to further expand their exchanges to date, and will also promote international exchanges of research results on nanotechnology and materials for realizing a sustainable society through cooperation between the two parties.

Development of He Plasma Ion Source

—High-efficiency ionization technology—

Shinji Itoh
Hitoshi Yamaguchi
Inorganic Chemical Analysis Group
Materials Analysis Station (MAS)

Glow discharge mass spectrometry (GD-MS) using argon (Ar) as the discharge gas was developed as a direct analytical method for high-sensitivity solid samples. GD-MS has come to be widely used in materials characterization method which enables high accuracy quantitative analysis from the main components to the mass ppb level and can be applied while the sample is in the solid state, requiring only simple sample preparation. However, because a large amount of energy is necessary for ionization of elements called gas-forming elements, such as O, N, as C, in comparison with other elements, it is known that the detected amounts are small (ionization efficiency is low). Furthermore, it was found that compound molecular ions called argide ions (MAr^+) cause overlapping (spectral interference) on the mass peaks of many elements, including zinc (Zn), molybdenum (Mo), and others.

Fig. 1: Helium glow discharge mass spectrometer.

We therefore developed a helium (He) plasma ion source to improve ionization efficiency and reduce spectral interference. The appearance of the device is shown in **Fig. 1**. In addition to the conventional vacuum exhaust system cryogenic pump, which stabilizes the ion source pressure and makes it possible to evacuate He, a turbo molecule pump was added, and the gas injection system was improved to a two-system type. Various conditions were studied, but in operation with a glow discharge parameter of 1 kV-3 mA, a stable glow discharge was obtained, and the relative sensitivity factor (RSF) was 2-3 orders of magnitude larger in comparison with Ar glow discharge. (RSF was obtained using the ratio of the ionic strength of each element to an internal-standard ionic strength for that element, as measured with a detector.) These results are shown in **Fig. 2**. An analysis of stainless steel was performed using RSF-values obtained by measuring 17 samples of certified iron and steel materials. As a result, good agreement with fluorescent X-ray quantitative analysis values and chemical analysis values was obtained for all elements, including not only the main component elements Cr and Ni, but also O and N, which are impurities, P and S, which are gas-forming elements, and others.

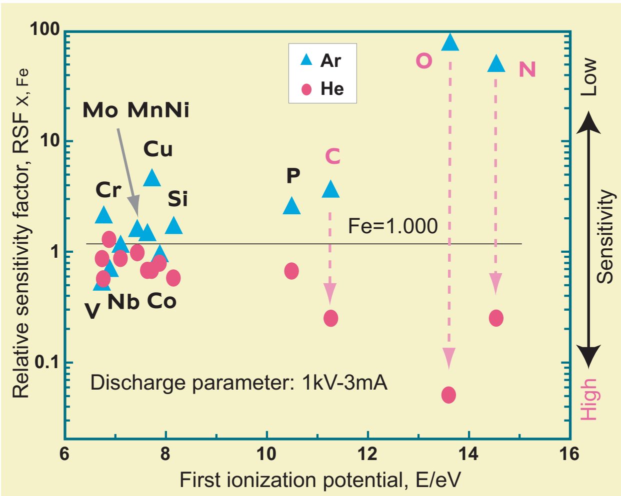


Fig. 2: Relation between ionization potential and RSF-value.

At present, the matrix ionic strength shows values approximately one order of magnitude smaller than in the case of Ar glow discharge. Therefore, as a future goal, we intend to improve the sensitivity of this method, including this point.

NIMS Signs MOUs with Two South African Governmental Research Institutes

CSIR-M&Mteck

In August 2003, the governments of Japan and the Republic of South Africa concluded an agreement on scientific and technical cooperation. A Japan-South Africa Scientific Forum was held in Pretoria, South Africa on May 10-14 of this year based on the agreement. On this occasion, the NIMS Materials Engineering Laboratory (MEL) exchanged MOUs with two South African governmental research institutes with which it already has exchanges, CSIR-M&Mteck (Council for Scientific and Industrial Research - Materials & Manufacturing Process Division) and Mintek (Council for Mineral Technology). With CSIR-M&Mteck, NIMS will cooperate in research on platinum-type coatings for Ni-base superalloys, while research co-operation with Mintek will involve refractory superalloys based on platinum group metals.

In addition to precious metals, South Africa has a wealth of mineral resources of various types, and research and development to enhance the added value of these resources is becoming an important national task. Thus, expansion to a wide range of cooperative relationships is expected in the future, including Cr alloys and other structural materials, functional materials such as catalysts and biomaterials, and nanotech-related cooperation.

MINTEK

Ultratrace Characterization by High-Selectivity Separation Method

Shin-ichi Hasegawa
Kunikazu Ide
Takeshi Kobayashi
Inorganic Chemical Analysis Group
Materials Analysis Station (MAS)

Development of the high-sensitivity inductively coupled plasma mass spectrometer (ICP-MS) made it possible to quantify trace elements in the ultratrace region at the ng/g level. However, this device is affected by the high concentration metal matrix and acids, reducing its measurement accuracy and causing a memory effect. It is therefore necessary to separate the matrix by pretreatment before introducing the sample solution into the device. The conventional separation methods are solvent extraction separation, in which the matrix or complex of the element to be analyzed is separated by extraction in an organic solvent, and ion exchange separation, but the organic solvents used in solvent extraction can be harmful to the environment and human body, depending on the type, and ion exchange requires considerable time.

As an extremely simple separation method, we conducted research on application of a solid-phase extraction method (**Fig. 1** and **2**), in which the element to be analyzed is adsorbed and separated using a solid-phase substance such as silica gel rather than an organic solvent (liquid phase).

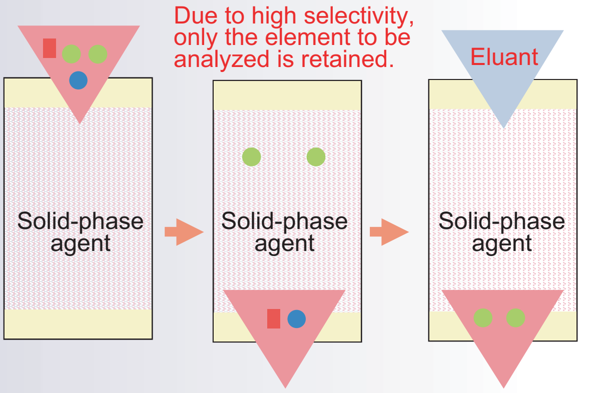


Fig. 1: Principle of solid-phase extraction.

In the wide sense, solid-phase extraction methods also include extraction using ion exchange resins. However, we used a chemically bonded silica gel as the solid-phase agent rather than a resin. As features, because the particle size (approx. 15-100 μm) is small in comparison with ion exchange resins, the gel has a large surface area, and a large quantity of sample solution can be separated rapidly using only a small quantity of the solid-phase agent (approx. 0.25-1 g). Moreover, because abnormal adsorption is slight in comparison with ion exchange resins, elution can be performed with a small quantity of eluant, and enrichment to high multiples is possible.

To date, we have established quantification methods for trace amounts of impurity elements in high purity metals including steel, aluminum, molybdenum, tungsten, and others using this separation technique.

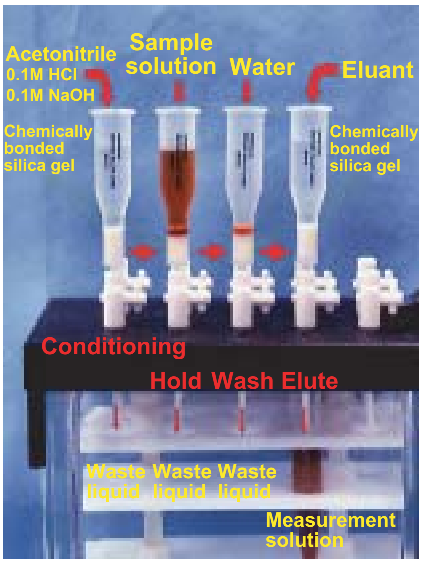


Fig. 2: Solid-phase extraction procedure.

In the future, we plan to expand this method to the isotope dilution (ID)/ICP-MS method, which is a standard analysis method, and improve its accuracy in ultratrace amount analysis of a large number of substances and materials.

NIMS Signs MOU with Nanjing University

On June 4, the NIMS Ecomaterials Center (EMC) signed a memorandum of understanding (MOU) on "Research on solar energy conversion and environmental purification materials" with the Dept. of Physics and Dept. of Materials Science and Engineering of Nanjing University in Nanjing, China. Nanjing University is one of the top-ranking universities in China and has educated many talented researchers, including a lot who have been engaging in research at NIMS. Based on the exchanges and the relationship of trust cultivated by the two institutions over past years, NIMS and Nanjing University agreed to personnel exchanges of researchers (including graduate school students), exchanges of research information and promotion of joint research programs.

MOU with University of Connecticut in the U.S.

On June 21, the Advanced Materials Laboratory (AML; Director-General, Dr. Mamoru Watanabe) and the Institute of Materials Science (IMS) at the University of Connecticut in the United States agreed to cooperate in research in the fields of "soft-bio/nanomaterials," and signed a memorandum of understanding. Under the MOU, the two sides agreed to a 5-year research cooperation relationship aimed at constructing biosensors and nanodevices based on novel principles by combining the research potential possessed by the IMS in the biotechnology and high polymer fields and the AML's nanomaterials and surface/interface self-assembly technologies. Based on the MOU, the IMS and NIMS intend to propose multiple joint research projects on bio/nanodevices to the American and Japanese government

Appointment of New Vice President

On July 15, 2004, Dr. Kenkichi Hirose, who had been serving as Director-General of the Administrative Office, Nuclear Safety Commission of Japan, was appointed as a new Vice President of NIMS, replacing an outgoing Vice President, Mr. Mikio Hattori. Dr. Hirose's term of office extends to March 31, 2005.

Biography

Doctor of Energy Science. Joined Science and Technology Agency (STA) in 1974 and engaged in science and technology administration for 30 years. Majored in Socio-Environmental Energy Science and completed the doctoral course at Kyoto University Graduate School of Energy Science. (1998)

Introduction of New Unit

High Voltage Electron Microscopy Station

Director-General: Kazuo Furuya
Deputy Director-General: Yoshio Matsui

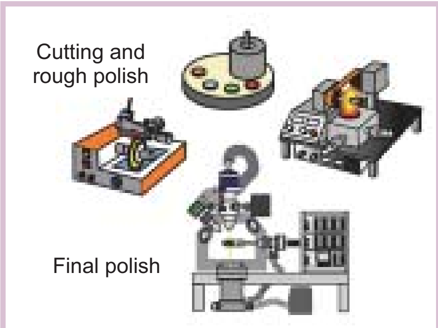
The High Voltage Electron Microscopy Station (HVEMS) has been established for the research and development (R&D) of HVEMs and related instrumentation for nano-characterization and study of material systems, and for utilization by users.

User Support Program for Nanotechnology

With In-situ, High-resolution and Analytical Electron Microscopy

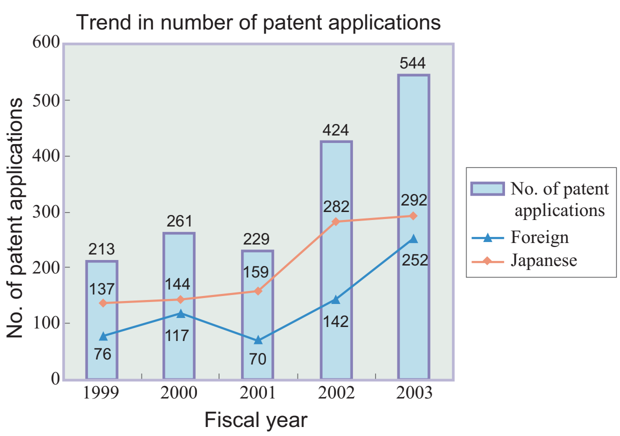
Technical Support Request → Sample Preparation → Atomic-level Observation → Data Analysis

NIMS is carrying out the user service for nanotechnology researchers with in-situ ion implantation, high resolution and atom-discriminating transmission electron microscopes (TEMs) under the nanotechnology user support project conducted by the Ministry of Education, Culture, Sport, Science and Technology (MEXT) .



For further information, please visit: http://www.nims.go.jp/hvems

NIMS Achieves Large Increase in Patent Applications



The basic principle of NIMS is "Materials are of value only when they are really used". NIMS therefore hopes to promote practical application by obtaining basic patents based on highly original basic research and transferring the technologies concerned to industry.

Since NIMS became an independent administrative institution in 2001, we have encouraged patenting of research results. Moreover, because technology is becoming increasingly internationalized, we are also putting considerable effort into international patent applications. As a result, the number of patent applications reached 544 in fiscal year 2003, or approximately 2.4 times the number two years earlier. This is equivalent to 1.2 patent applications/year for each full-time NIMS researcher. As of the end of FY 2003, a total of approximately 2,300 Japanese patents had been granted.

In the future, we also plan to further improve the quality of patents. NIMS will continue to be a good partner to industry and invites interested parties to contact us regarding patents and licensing.

[Intellectual Property Office: M-O@nims.go.jp ,(Fax) +81-29-851-3888]

Interdisciplinary Research: Key for Environmental Materials

Nitin K. Labhsetwar (NEERI, India)
Visiting Research Fellow (Jun, 2004-Jul, 2004)
Electroceramics Group, Advanced Materials Laboratory (AML)

[NEERI Director and scientists visiting NIMS (author: third from the left)]

Development of new and advanced materials is imperative to resolve environmental problems as well as to achieve sustainable development. The ongoing R&D in materials science all over the world therefore, focuses on innovative approaches to develop various materials for their possible applications in fairly complex environmental problems. This does not only involve scientific capabilities in material design and synthesis; it is equally important to know the exact requirements and practical conditions of material application. Obviously, this was the main reason for research collaboration between NIMS and National Environmental Engineering Research Institute (NEERI), India.

While working with NEERI, I realized the complexity and diversified requirements of materials for different environmental applications, it was indeed a pleasure to experience the various dimensions of truly interdisciplinary materials research at NIMS.

We are presently focusing on catalytic and photocatalytic materials for environmental applications like- VOCs control, diesel emission control, water splitting, methane combustion etc. Working with the Electroceramics group has always been a pleasure and I am also impressed with the accessibility of other researchers as well as various research facilities at NIMS. It is indeed good to see the NIMS research priorities giving due recognition to material development for environmental applications. I am sure, with its immense capabilities in materials research, NIMS will contribute significantly towards environmental applications.

Life Enriching Experience

Joka Buha (University of New South Wales, Australia)
Joint International Graduate School Program
(Apr. 2004 - Jul. 2004)
Metallic Nanostructure Group
Materials Engineering Laboratory (MEL)

[With colleagues, back, third from the right]

My relatively short and purely work focused visit to Japan has transformed and regenerated the way I experience life. While I was preoccupied with chasing clusters in aluminium alloy using a three dimensional atom probe, my stay at NIMS refreshed my life on a professional, as well as a more personal level.

The care shown for foreign scientists at NIMS (accommodation, language, and pretty much everything else taken care of) allowed me to give all my attention to my research. Working with a large group of brilliant young scientists, wonderful and cheerful people, was very rewarding and above all stimulating. This reminded me of why I wanted to be a scientist in the first place.

Living and working in a miraculously different and beautiful country such as Japan, was a truly exceptional personal experience for me. Before I realized it, I was embraced by the genuine kindness and warmth of the Japanese people. The differences that exist between Japan and the culture I was more accustomed to were most edifying and something that broadened my perception of life. A truly life transforming and enriching experience indeed.

Independent Administrative Institution
National Institute for Materials Science

NIMS NOW International is a monthly newsletter of NIMS which provides the latest research activities on substances and materials, and notification and report of events for international readers.
For free subscription and download, please visit "NIMS NOW International online" at:
http://www.nims.go.jp/eng/news/nimsnow/

Publisher: Dr. Masatoshi NIHEI
Since: July, 2003

Contact Details:
Naoko ICHIHARA (Ms.)
Public Relations Office, NIMS
1-2-1 Sengen, Tsukuba
Ibaraki 305-0047
JAPAN
Phone: +81-29-859-2026
Fax: +81-29-859-2017
inquiry@nims.go.jp
http://www.nims.go.jp/