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Inspire the Next

Measurement and Analysis Technologies for Future Science and Social Innovation

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From the Editor

Measurement and analysis technologies contribute to science and technology by enabling new discoveries such as the deoxyribonucleic acid (DNA) double helix and the detection of neutrinos. They also deliver numerous benefits in our daily lives, such as conducting clinical analyses at a health check and testing the composition of food. In industry, they are used in research and development and in process and quality control. Advanced measurement and analysis technologies are recognized as promoting innovation and boosting scientific and technical competitiveness.

In these ways, measurement and analysis technologies can be thought of as underpinning the progress of science and society. This issue of *Hitachi Review* presents the latest trends and solutions in measurement and analysis from numerous fields, including the environment and renewable energy, new materials, life science, and electronics.

In Expert Insights, Prof. Daisuke Shindo, a professor at Tohoku University who is also team leader of Emergent Phenomena Observation Technology Research Team at the National Research and Development Institute, RIKEN, has contributed an article about his expectations for the world's first atomic-resolution holography electron microscope, which was developed by Hitachi with support from the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

In Technotalk, leaders active in leading-edge research talk about the latest trends in the field of measurement and analysis technology and prospects for the future. We also have articles, Special Contributions, about work being undertaken in partnership with Hitachi covering the latest university research. Prof. Dr. Max Haider from Corrected Electron Optical Systems GmbH (CEOS) of Germany also contributes an article about joint development with Hitachi dealing with the aberration corrector that enabled the atomic-resolution holography electron microscope to achieve world-leading resolution.

Other articles describe various products and solutions for measurement and analysis from Hitachi that satisfy the latest requirements. As requirements become more diverse, measurement and analysis technologies are being called on to deliver not only higher performance but also new functions for specific purposes or ways of integrating or merging different measurement and analysis techniques. The articles in this issue cover numerous initiatives of this nature.

Through collaborative creation, Hitachi is working to develop new businesses and services by establishing a common understanding of the challenges facing customers and partners. Above all else, measurement and analysis technologies are closely linked to their requirements, and Hitachi collaborates with key opinion leaders to create leading-edge technologies and solutions.

I hope that this issue of *Hitachi Review* will foster understanding of Hitachi's measurement and analysis technologies and its work on developing products and solutions, and will provide us all with opportunities for the collaborative creation of new value.

Editorial Coordinator,
"Measurement and Analysis Technologies for Future Science and Social Innovation" Issue

Toshio Masuda, P.E.Jp

Chief Engineer
Planning and Facilitating Department
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Hitachi High-Technologies Corporation (serving as editor at time this issue was written)

Measurement and Analysis Technologies for Future Science and Social Innovation

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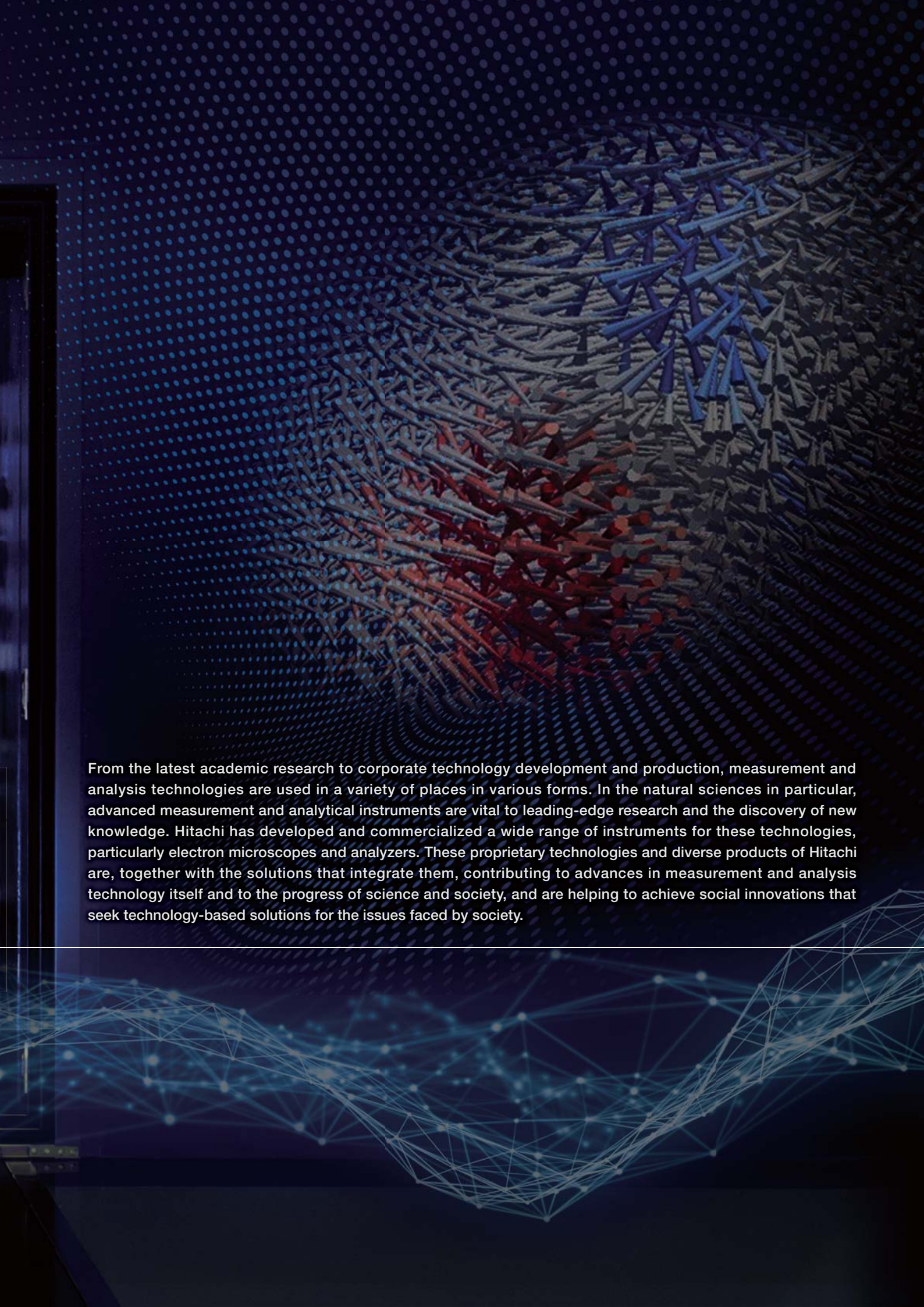

From the latest academic research to corporate technology development and production, measurement and analysis technologies are used in a variety of places in various forms. In the natural sciences in particular, advanced measurement and analytical instruments are vital to leading-edge research and the discovery of new knowledge. Hitachi has developed and commercialized a wide range of instruments for these technologies, particularly electron microscopes and analyzers. These proprietary technologies and diverse products of Hitachi are, together with the solutions that integrate them, contributing to advances in measurement and analysis technology itself and to the progress of science and society, and are helping to achieve social innovations that seek technology-based solutions for the issues faced by society.

Expert Insights

Expectations for Atomic-resolution Holography Electron Microscope

Prof. Daisuke Shindo, Dr. Eng.
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
Head of Center for Advanced Microscopy and Spectroscopy

Graduated in nuclear engineering from the School of Engineering at Tohoku University in 1977 and completed a doctoral program at Graduate School of Engineering at Tohoku University in 1982. Appointed as Research Associate at Institute for Materials Research, Tohoku University in 1982, Associate Professor at Institute for Advanced Materials Processing, Tohoku University (previously Research Institute of Mineral Dressing and Metallurgy) in 1992, and Professor at Institute for Advanced Materials Processing, Tohoku University (since renamed Institute of Multidisciplinary Research for Advanced Materials) in 1994. He has also served as Team Leader of Emergent Phenomena Observation Technology Research Team at RIKEN since 2012.
Doctor of Engineering. His specialty is the measurement of electromagnetic fields using electron interference.

The atomic-resolution holography electron microscope project, launched in March 2010 by the late Akira Tonomura under the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program), was completed last year. Overcoming numerous difficulties, not least of which was the Great East Japan Earthquake, Dr. Tonomura was, in accordance with his own wishes, succeeded within Hitachi by Nobuyuki Osakabe and Hiroyuki Shinada, and the project culminated in a 1.2-MV ultra-high-voltage electron microscope that combines atomic resolution with the ability to image electromagnetic fields. Although a number of ultra-high-voltage electron microscopes have been constructed in the past, mainly in Japan, I offer my sincere congratulations for achieving the world's first ever ultra-high-voltage holography electron microscope with an electron interference function, and featuring extremely high voltage stability and an aberration corrector. Of the four fundamental forces of the natural world (strong force, weak force, electromagnetism, and gravity), it is electromagnetism that accounts for most of the phenomena with which we are familiar, particularly interactions on the nano- to micro-scales. Electromagnetism has its origins in electromagnetic fields, and the public announcement of the ability to image electromagnetic fields with world-leading resolution is highly significant in terms of Japan maintaining its role as a world leader in the field of science and technology.

The FIRST Program has also actively promoted applied research into the observation of electromagnetic fields using holography electron microscopes. I myself have received FIRST funding for applied research into such subjects as advanced materials and biological samples using the 300-kV holography electron microscope at the National Research and Development Institute, RIKEN. While charge buildup due to the discharge of secondary electrons is known to occur when non-conductive samples such as biological material are viewed under an electron microscope, it has recently been discovered that when this buildup of charge becomes large, the previously discharged secondary electrons are attracted back to the sample, and that the formation of stable orbital configurations in the vicinity of the sample surface can be imaged by detecting the

disturbance in the electric field due to the movement of electrons. Moreover, the late Shinji Aizawa of Hitachi High-Technologies Corporation joined my team at RIKEN to engage in further research, where he undertook numerous precise and delicate experiments and succeeded in obtaining sharp and dynamic images of the collective motion of electrons that had progressively built up on the surface of a biological sample. This reinforced my strong impression of the very high technical capabilities of Hitachi researchers.

Underpinned by the high level of technical capabilities passed on from one Hitachi researcher to another and shared between them, the atomic-resolution holography electron microscope is recognized for how, in the future, it will continue to uncover information on electromagnetic fields at the atomic level that is important for understanding the electromagnetic characteristics of various types of advanced devices. In addition to this information on electromagnetic fields, I look forward to the microscope also being utilized in the near future for the analysis of complex quantum phenomena that have to date remained unexplained through the tracking of interactions between atomic lattices imaged with world-leading resolution and electrons detected as disturbances in electric fields.

Technotalk

Use of Interdisciplinary Knowledge to Improve Measurement and Analysis Technology

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Tatsuo Ushiki, M.D., Ph.D. Dean, Faculty of Medicine; Dean, Institute of Medicine and Dentistry; Professor of Microscopic Anatomy, Niigata University
Masaaki Sugiyama, Dr. Eng. Specially Appointed Professor, Graduate School of Engineering, Osaka University
Sukehiro Ito General Manager, Electron Microscope Systems Design Department, Science Systems Product Division, Science & Medical Systems Business Group, Hitachi High-Technologies Corporation
Ryuichiro Tamochi General Manager, Science Systems Business Development Department, Strategic Planning Division, Science & Medical Systems Business Group, Hitachi High-Technologies Corporation
Hiroyuki Shinada, Ph.D. Senior Chief Researcher, Center for Exploratory Research, Research & Development Group, Hitachi, Ltd.

Part of the foundations of science and industry, measurement and analysis technologies are used in a wide variety of fields, including the development of new materials, biology, electronics, the environment, and renewable energy. Hitachi has contributed to the development of industry and society through measurement and analysis technology and its applications, having had a long involvement in instrumentation, electron microscopes, spectrophotometers, and other such devices. Along with strengthening its core technologies and expanding its product range, Hitachi is also pursuing collaborative creation and open innovation with customers in specialist fields, utilizing measurement and analysis technology to provide extensive support everywhere from the latest academic research to industry.

Enabling Dynamic Observation and Establishing Platforms

Shinada: The abilities to observe, measure, and analyze are fundamental to science and industry, and society is underpinned by the widespread use of measurement and analysis technology everywhere from advanced research and development to the factory floor. Today we have invited a number of experts in the fields of materials development, medicine, and biology. I would like to start by asking each of you to summarize the contribution of measurement and analysis technology and the latest trends in your own field.
Kitagawa: In my own specialty of materials science, capabilities like in situ observation and "operand measurement*" are becoming increasingly important. Overseas, in particular, progress is being made on the development of methods such as performing surface observations under an electron microscope when hydrogen or other gases are injected and react with a catalyst, or observing the condition of materials inside a battery during use. While such techniques are also increasingly being adopted in Japan, this is a field where greater effort is still needed.

Work is also proceeding on materials informatics whereby data analysis techniques are applied to materials design, with a database of materials information being created, primarily through the National Institute for Materials Science (NIMS). While progress has already been made on the fusion of materials science and design techniques, this use of data analysis and information processing is likely to become essential in the future. Advanced measurement and data analysis techniques are seen as holding the key to future leading-edge research.

Another area where Japan needs to make a greater effort is in the establishment of platforms. Japan has a large number of joint research facilities, including supercomputers, synchrotrons, neutron beam generators, large electron microscopes, and research facilities for strong magnetic fields and nuclear magnetic resonance (NMR). While these serve as sites for undertaking basic research and other advanced studies, there is a need to proceed with the development of research platforms by establishing hubs and networking them to improve the international competitiveness of science and industry.
Ushiki: In medicine and biology, electron microscopes have made a major contribution to the progress of cell biology. It is only thanks to the resolution of electron microscopes that we have been able to observe the

* Measurement and analysis of catalysts and devices under actual operating conditions.

structures of viruses and of the Golgi apparatus, mitochondria, and other cell components, and without this ability there would be no modern biology. Meanwhile, while it builds on knowledge of cell biology acquired by electron microscopes, the focus in recent times has been on fields such as molecular biology working with molecules and genes that can be labeled by optical microscopy.

Nevertheless, this does not mean that electron microscopes will not be used in the future as there remains a need for reliable shape observations. The problem with electron microscopes is that, for all the high resolution they have, their ability to view shapes is not accompanied by being able to view color or function. Instruments such as confocal microscopes and two-photon microscopes that use laser light have become more widely used recently, and optical microscopes have the advantage that they can be used for dynamic observation of living cells. If the challenge of being able to view moving specimens can be overcome, then we can expect to see greater uses for electron microscopes in medicine and biology.

Shinada: The establishment of platforms spoken about by Professor Kitagawa is also important for open innovation. Hitachi, too, is actively seeking to collaborate and cooperate with universities, research institutions, and other companies. In this context, I would like to ask Professor Sugiyama, a leader in collaboration between industry and academia, for his thoughts on open innovation.

Sugiyama: Having worked in steel industry laboratories researching ferrous materials up until March 2015, I have taken up a joint research chair post at Osaka University. It is important to work out how alloying elements distribute themselves through the steel we produce to achieve the desired mechanical properties, something that would be impossible without the use of electron microscopes and other analytical equipment.

Recent years have seen an intensification of development competition in materials with high strength, with emerging economies becoming more prominent. This has forced companies and universities to engage in joint research, even more so than in the past, with extensive knowledge of materials science being needed to ensure that the end products have specific mechanical and other physical properties in actual use. This has been accompanied, however, by a shift away from the contract research used in the past, toward more integrated research efforts in order to obtain timely and effective solutions to problems. Naturally, this is an important part of open innovation, and we can also see this as a trend toward companies and universities acting together to develop human and technical resources in the short and medium terms. Our plans for joint work go beyond basic materials science to include research on new characterization techniques for overcoming the deficiencies of existing

Hiroshi Kitagawa, Ph.D.

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Graduated from the Faculty of Science at Kyoto University and undertook post-doctoral work in chemistry at its Graduate School of Science. After posts that included assistant professor of chemistry at the University of Tsukuba and professor of chemistry at the Graduate School of Science at Kyushu University, he took up his current position in 2009. Doctor of Science. His appointments include a councilor of the Japan Society of Coordination Chemistry.

Tatsuo Ushiki, M.D., Ph.D.

Dean, Faculty of Medicine; Dean, Institute of Medicine and Dentistry; Professor of Microscopic Anatomy, Niigata University

Graduated from the School of Medicine, Niigata University and obtained a doctorate from the Graduate School of Medicine. Following appointments that included associate professor at Hokkaido University, he was appointed professor at the School of Medicine, Niigata University in 1995, and to his current position in 2014. Doctor of Medicine. His specialty is microscopic anatomy. His publications include an "Introduction to Histology" (published by Nankodo, in Japanese).

analytical equipment.

Shinada: Collaboration between industry and academia is important for equipment development, just as much as in basic science. Professor Ushiki, you have worked with Professor Futoshi Iwata on the Faculty of Engineering at Shizuoka University, Hitachi High-Technologies Corporation, and others on the development of a scanning electron microscope (SEM) that can be used for realtime three-dimensional (3D) imaging and a high-resolution 3D monitor that can be viewed with the naked eye, the work being undertaken as part of a Japan Science and Technology Agency (JST) program for the development of advanced measurement and analytical techniques and equipment. What do you see as the key factors in the success of collaborations like this?

Ushiki: Because our interests in our own specialties do not always overlap with corporate development objectives, it is important that both sides make allowances. The development of analytical equipment for solving highly specialized problems needs to be approached with patience as a number of steps are worked through. Achieving this requires that you find partners with whom you can develop mutual respect and share goals. Success comes from having people who appreciate other fields and who can act as go-betweens.

Kitagawa: As you say, building the right environment is important. The need for data analysis and information processing was mentioned earlier, but there is a significant gap between specialists in that field and materials science researchers. It may be that what is needed is a way to bring together people with an interest in each other's work so as to develop fields that tie together different disciplines in this way along with people who understand both sides.

Moving from Equipment to Solutions

Shinada: Now that you have told us about the latest developments regarding analytical equipment, what are your comments on the work of Hitachi High-Technologies?

Ito: With regard to the "operand analysis" practices spoken of by Professor Kitagawa, development is underway aimed at using transmission electron microscopes (TEMs) for this purpose. Looking at measurement and analysis systems in overview, Hitachi has for some years been working to strengthen its lineup of TEMs, SEMs, and focused ion beam (FIB) instruments. In the field of materials development referred to by Professor Sugiyama, for example, we have supplied the materials industry with a field emission scanning electron microscope (FE-SEM) fitted with a Schottky emitter electron gun that was released in 2014. We have also contributed to society, with the realtime 3D-SEM we developed in partnership with Professor Ushiki, which subsequently launched

Masaaki Sugiyama, Dr. Eng.

Specially Appointed Professor, Graduate School of Engineering, Osaka University

Graduated from the Division of Materials Physics, School of Engineering Science, Osaka University, and obtained a doctorate from its Graduate School of Engineering Science. After joining Nippon Steel Corporation (now Nippon Steel & Sumitomo Metal Corporation), he was engaged in research into first ceramics, and then steel. He was involved in technology planning and the study of material microstructure control, primarily electron microscope technology. He was appointed to his current position in 2015. Doctor of Engineering. He is a member of the Japanese Society of Microscopy (JSM), The Japan Institute of Metals and Materials, and the Iron and Steel Institute of Japan.

Sukehiro Ito

General Manager, Electron Microscope Systems Design Department, Science Systems Product Division, Science & Medical Systems Business Group, Hitachi High-Technologies Corporation

Joined Hitachi Naka Seiki, Ltd. in 1984 where he worked on the design and development of scanning electron microscopes. He is currently engaged in managing the design and development of electron microscopes and focused ion beam milling machines. He is a member of the JSM.

on the market (with more than 180 instruments shipped). Along with high-end products, we are also seeking to expand our user base by developing SEMs, TEMs, and FIB instruments that anyone can use.

In the future, it will be necessary to supply not only instruments but also solutions and systems. We are also launching initiatives aimed at identifying requirements in consultation with users and academics at universities and research institutions. For example, we have been looking into live correlative light and electron microscopy (CLEM), a bioimaging technique that is capable of structural analysis at the molecular level using both a fluorescence and an electron microscope, and we are working on joint development with National Research and Development Institute, RIKEN, to build systems that are easier to use.

Tamochi: What is important when it comes to solutions is to provide total support that extends from sample preparation to measurement and subsequent tasks. Accordingly, we established our Tokyo Solution Laboratory in February 2011. By providing a venue that is closer to customers for holding demonstrations and hands-on training on key products, we are seeking to improve user convenience and strengthen collaborations with universities and research institutions in Japan and elsewhere.

In 2012, Hitachi High-Technologies acquired SII NanoTechnology Inc., an analytical equipment business, and re-established it as Hitachi High-Tech Science Corporation. This enabled us to add surface analyzers, scanning probe microscopes (SPMs), and coherence scanning interferometers to our product lineup. We are drawing on the resulting synergies to devise systems that can use an SPM and SEM in tandem to combine surface images with localized physical properties analysis, for example.

Hitachi High-Tech Science has X-ray analyzers and is working on deploying this general-purpose technology in specific purpose instruments such as those for detecting contaminants in food or those used in quality control of lithium-ion batteries. Our aim is to promote innovation through analytical equipment by utilizing core technologies for electron beams, ion beams, spectrometry, and X-ray analysis to supply solutions to a wider range of customers.

Kitagawa: Nowadays, paying attention to feedback from users is as important as the technology itself when it comes to overcoming competition from overseas suppliers of analytical equipment.

Shinada: In this respect, it is important to take note of open innovation. For Hitachi as a whole, open innovation and collaborative creation are key concepts as we go about our Social Innovation Business, research into advanced technologies, and product and service development. Accordingly, we have reorganized our research laboratories to strengthen collaborative-creation with customers and customer-

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Joined Hitachi Instrument Engineering Co., Ltd. in 1984 where he worked on the development of application technology for scanning electron microscopes. He is currently engaged in business strategy for scientific system products. He is a member of the JSM and The Surface Science Society of Japan.

Hiroyuki Shinada, Ph.D.

Senior Chief Researcher, Center for Exploratory Research, Research & Development Group, Hitachi, Ltd.

Joined Hitachi, Ltd. in 1985 where he worked initially at the Central Research Laboratory and then in the research and development of semiconductor production and inspection machines based on electron microscopy and on electron sources and electron guns. He is currently engaged in development and applied research into holography electron microscopes. Doctor of Engineering. He is a member of the JSM, The Japan Society of Applied Physics, and the Society of Instrument and Control Engineers.

inspired research and development.

Sugiyama: While it is vitally important to take account of user feedback in product development, as technology advances, it is also essential that a variety of researchers share their core knowledge in order to make the breakthroughs for the next generation of technologies. I believe this is why a growing importance is being placed on open innovation across different companies. Rather than companies in the same industry, I believe that the key lies in the fusion and integration of knowledge from different disciplines and industries, and that universities can serve as go-betweens to make this happen.

Overcoming New Challenges by Incorporating Interdisciplinary Knowledge

Shinada: I see collaborative creation between industry, government, and academia growing in importance as a way to create innovative measurement and analysis technology.

Tamochi: One of the most important aspects of measurement and analysis technology is the analysis of data obtained through observation. The higher the level of the object under observation, the higher the level of data interpretation will become, and therefore it is necessary to incorporate domain-specific knowledge.

Sugiyama: In the microstructure of an observed object can appear completely different when viewed from a slightly different angle in TEM. To obtain a quick solution, it is important that there is a sense of solidarity between experts in measurement and analysis technology and those in materials development who need to use this technology. Furthermore, it may be possible to discover facts that were previously hidden by combining techniques from big data analytics to view large data sets from different perspectives. In this case, it will also be necessary to educate researchers to be able to find something new in overlooked data or noise, making it important to find ways to bring people together by establishing hubs and platforms.

Ushiki: In biology, whereas imaging has been important for qualitative assessment, I believe we are well behind when it comes to ways of using image data from electron microscopes to perform the statistical and quantitative analyses that have become necessary in recent times. In this respect, while we may talk about analytical equipment, there are numerous aspects in which *measurement* is not the right word.

Shinada: Hitachi High-Technologies supports the precision measurements required in semiconductor manufacturing by developing the measurement SEM inspection systems used for dimensional measurement. The know-how built up in this field has the potential to be useful in the development of quantitative techniques for image analysis. It could also lead to breakthroughs in the application of big data analytics and artificial intelligence (AI) to microscope images.

Kitagawa: My greatest concern at the moment is that, while scanning transmission electron microscopes (STEMs) are very useful instruments, they are only able to focus on a narrow range. In the case of metals, for example, I was interested in high-entropy alloys with a large number of alloying elements and wanted to use STEM energy dispersive X-ray analysis (STEM-EDX) to gain a 3D view of the distribution of elements in a nano-sized grain, but the analysis was complicated by problems with focusing the STEM and with overlapping EDX characteristic X-rays. I believe there must be a way of doing it, whether it be a physical solution or using a data analysis technique such as multivariate analysis, and I hope you can show me what it is.

Ushiki: Perhaps you can deal with your focusing problem by taking lots of images with different focuses and merging only those parts that are in focus.

Tamochi: That's right. In-lens SEM incorporates a technique whereby a series of images are taken automatically with different focuses and only the sharp parts of each image are overlaid, so that is an approach you could try.

Ito: To deal with EDX sensitivity problems, we are working with Dr. Toru Hara of NIMS and others on the development of a micro-calorimeter with a transition edge sensor (TES) using a technique from Hitachi High-Tech Science. If this instrument can be successfully developed, it should prove useful for precise nano-scale composition analysis by providing much higher energy resolution than conventional EDX systems.

Kitagawa: I will look forward to that. In materials science, it is known that, in between the microscopic world at the molecular level and the macro world of visible crystals, structures in the mesoscale range have an influence on material properties. However, there are numerous difficulties with the techniques for viewing at this scale, and so I see much potential for the use of electron microscopes.

Shinada: Even as science progresses, there remain numerous areas that are yet to be understood, so to help address these challenges is essential that the field of measurement and analysis adopt a wide range of technologies, knowledge, and people.

Hitachi has been working on holography electron microscopes for a long time, particularly the late Akira Tonomura, who was recognized with the title "Fellow of Hitachi, Ltd." A holography electron microscope with an accelerating voltage of 1.2 MV developed by a project entitled "Development and Application of an Atomic-resolution Holography Electron Microscope," which was supported by the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program), achieved world-leading resolution of 43 pm in December 2014. It is hoped that the microscope will make a major contribution to progress in basic science in addition to its use, not just at Hitachi, but also in Japan's leading-edge development of functional materials. I invite you all to submit any research projects you might have.

Sugiyama: It is important to make the best equipment in the world. The success in technology attracts people and breeds confidence in the field. New technical innovations are invariably needed for world-leading achievements, and the knowledge you gain in the process often proves its worth over and over again in the future.

Ushiki: Any improvement in resolution, even if only a small increment, makes it possible to view things that could not previously be seen. You also need to make an effort to take advantage of this.

Kitagawa: Japan's measurement and analysis technology is in itself at a high level by world standards, and it is important that we continue to move toward the high end. On the other hand, an overemphasis on specifications can also result in technology being difficult to use. What is needed is to combine top-level technology with user-friendly features that enable all users to achieve a certain level of performance.

Ito: That's right. Our aim is to contribute to advances in the measurement and analysis platforms that underpin science and industry by improving ease-of-use as well as by taking on new challenges in pursuit of performance, quality, and reliability.

Shinada: It has become clear to me that ways of establishing horizontal links and developing human resources are just as important as delving into the specialist technologies and fields in which Japanese people have expertise.

Our intention is to contribute to progress in society and science through open innovations in which measurement and analysis play a pivotal role, while also continuing to develop the measurement and analysis technologies of Hitachi. Thank you for your time today.

Overview

Hitachi's Measurement and Analysis Technologies for Future Science and Social Innovation

Ryuichiro Tamochi
Sukehiro Ito
Katsumi Hayakawa
Toshio Masuda

MEASUREMENT AND ANALYSIS TECHNOLOGIES THAT UNDERPIN SOCIAL INNOVATION

Measurement and analysis, meaning the ability to observe, measure, and analyze, are essential to the progress of science and society. Many new scientific discoveries were brought about by advances in measurement and analysis technologies, and they are collectively described as the "Mother of Science." In industry, a wide range of measurement and analysis technologies are used in everything from research and development to actual production where they underpin things like the development of new technologies and improvements in product quality. Measurement and analysis serve as a platform for innovation and the creation of innovative solutions, contributing to the progress of society by advancing a variety of fields such as the environment, renewable energy, new materials, life sciences, and electronics.

Hitachi is working on developing measurement and analysis technologies and on enhancing products and solutions, particularly electron microscopes and analyzers. Moreover, Hitachi is seeking to make advances in measurement and analysis technologies and to contribute through the latest such technologies to the progress of science and society by working not only in-house, but also through collaborative creation with universities, research institutions, and other companies in Japan and elsewhere.

Hitachi is currently promoting its Social Innovation Business, which seeks to create a safe and secure way of life by dealing with the problems of customers and society through solutions that combine advanced information technology (IT) with social infrastructure. Measurement and analysis technology underpins the achievement of social innovation by serving as a foundation for the progress of both IT and social infrastructure.

REQUIREMENTS OF SOCIETY AND DEVELOPMENT OF TECHNOLOGIES AND SOLUTIONS FOR MEASUREMENT AND ANALYSIS

Hitachi entered the measurement and analysis systems business in the 1960s, with involvement in precision measurement instruments such as flow meters, spectrophotometers[(a)], mass spectrometers[(b)], and various types of electron microscopes, including transmission electron microscopes [TEMs[(c)]], scanning electron microscopes [SEMs[(d)]], and field-emission scanning electron microscopes [FE-SEMs[(e)]]. Hitachi has a history of supplying leading-edge measurement and analysis technology by developing new measurement techniques such as non-destructive testing that use methods such as X-ray or ultrasound,

(a) Spectrophotometer
An instrument for determining the proportion of light absorbed by a sample at different wavelengths by directing light of particular wavelengths at the sample and measuring how much of the light is transmitted. Spectrophotometers are widely used to measure and view things like solution concentrations for liquid samples and physical properties or molecular structure for solid samples.

(b) Mass spectrometer
A mass spectrometer is used to identify or quantify the content of a sample by ionizing it (by a variety of means), breaking it apart electromagnetically, and detecting the constituent atoms and molecules. Many different types of mass spectrometers with different ionization or detection techniques are available to suit different end uses.

(c) TEM
Transmission electron microscope. A TEM is a type of electron microscope that passes a beam of accelerated electrons through a thinly sliced sample and directs the electrons scattered or refracted by the atoms in the sample toward a fluorescent screen or charge-coupled device (CCD) camera to form an electron beam diffraction pattern or TEM image. TEMs can perform high-resolution imaging of the internal structure of materials.

scanning probes, synchrotron radiation applications, non-invasive optical biometrics, and by improving their performance and making other enhancements.

In response to market requirements, Hitachi has also developed products and solutions that provide general-purpose measurement and analysis technologies in the form of special-purpose instruments. Examples include measurement SEMs(f) that are based on an FE-SEM and are used for measuring the dimensions of semiconductor devices, and automated clinical analyzers that are based on spectroscopic analysis technologies. Because these special-purpose products incorporate automation and operational improvements that make it easy to perform high-quality measurement and analysis, they have made a major contribution to industrial progress and to a safe and secure way of life through widespread use in areas such as manufacturing and healthcare.

Amid a shift from focusing on performance to focusing on objectives, there has been an increase recently of field-specific demands. For the development of new materials, there is demand for "operand measurement," meaning the measurement and analysis of catalysts or devices in operation, while in medicine and life sciences there is a demand for the integration and interoperation of electron microscopes that can obtain detailed morphological information from live tissue using optical measurement techniques for obtaining color information. In response to these demands, Hitachi is working on the development of new measurement and analysis technologies and new functions and solutions.

As the requirements, the objects to be measured, and the reasons for doing so become more diverse, it is important to have a wide range of measurement and analysis methods and to be able to put together an appropriate mix of equipment and techniques to suit specific objectives or requirements. In 2013, Hitachi High-Technologies Corporation consolidated the analytical instruments business within Hitachi by acquiring full ownership of SII NanoTechnology Inc. from Seiko Instruments Inc. and forming Hitachi High-Tech Science Corporation. In addition to consolidating a high level of analysis technology built up in fields such as scanning probe microscopes [SPMs(g)], optical measurement, ion optics, mass spectrometry, and thermal analysis, Hitachi High-Tech Science also intends to satisfy diverse requirements using linkage systems that integrate different measurement and analysis instruments, including electron microscopes. It has established a demonstration room equipped with various instruments that provides what is needed to run demonstrations of these instruments working together, and that it is hoped will serve as a venue for collaborative creation with customers.

DEVELOPMENT OF LEADING-EDGE PRODUCTS AND SOLUTIONS THROUGH COLLABORATION

Development of Atomic-resolution Holography Electron Microscope

Electron microscopes can observe, measure, and analyze with high resolution. The instrument that has taken this high resolution to the greatest extreme is the atomic-resolution holography electron microscope(h). With funding from the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program), Hitachi launched a project to develop a holography electron microscope with

(d) SEM
Scanning electron microscope. An SEM is a type of electron microscope that obtains a magnified image by scanning a tightly focused beam of primary electrons from an electron source (a device that emits a beam of electrons) across a sample and using a detector to detect the resulting electrons, which may be secondary electrons emitted by the sample or reflected electrons that are emitted when the incident electron beam changes direction inside the sample. SEMs can view the three-dimensional structure of material surfaces with high resolution.

(e) FE-SEM
Field-emission scanning electron microscope. Field emission (FE) means the high-density emission of electrons that occurs when a high voltage is applied to the tip of a sharply pointed negative electrode (electric field emission probe) at ultra-high vacuum. FE-SEMs are SEMs that use this phenomenon for their electron source, and are characterized by the high resolution that results from the very high intensity of the FE electron source.

(f) Measurement SEM
Also known as a critical dimension scanning electron microscope (CD-SEM). Measurement SEMs are mainly used for quality management on production lines for semiconductor and other electronic devices. A measurement SEM incorporates an SEM (originally intended as an observation instrument) that has been designed specifically for the measurement of microcircuit pattern dimensions by equipping it with the repeatability and calibration functions required for use as a measurement instrument.

(g) SPM
Scanning probe microscope. The general term for microscopes that performs surface profile observations and physical property analysis by scanning a small needle-sharp probe over a sample near its surface to determine physical quantities (including tunnel current, interatomic forces, friction, and magnetic force) that act between the probe and sample. Common forms of SPM include scanning tunneling microscopes (STMs) and atomic force microscopes (AFMs).

(h) Atomic-resolution Holography Electron Microscope
Electron beam holography forms an image of the interference pattern created by an electron beam behaving as a wave. Similarly, a holography electron microscope performs electron beam holography in an electron microscope. It can observe and measure the three-dimensional shape of the material and the microscopic electric and magnetic fields inside the material or in empty space by generating an electron hologram from the interference between the electron beam that passes through regions where the sample is present and the electron beam that passes through regions where the sample is absent. Because the holography electron microscope developed by Hitachi has sufficient resolution to resolve individual atoms, it is called the atomic-resolution holography electron microscope.

an accelerating voltage of 1.2 MV in March 2010. After overcoming many difficulties, this succeeded in achieving world-leading resolution of 43 pm in December 2014[1] (see Fig. 1).

The atomic-resolution holography electron microscope not only features high resolution, it can also measure electromagnetic fields with atomic resolution. This means it has potential for use in advancing the development of new materials that can help overcome energy and environmental problems, such as the development of high-performance magnets for hybrid or other electric vehicles, and contribute to the progress of basic science through the development of groundbreaking new materials. By using the atomic-resolution holography electron microscope as an advanced measurement and analysis platform and sharing it with others from outside of Hitachi, Hitachi intends to proceed with open innovation in collaboration with leading research institutions in Japan and elsewhere*.

Fig. 1—Atomic-resolution Holography Electron Microscope. Hitachi achieved world-leading resolution of 43 pm in December 2014 by incorporating a spherical aberration corrector onto an ultra-high voltage electron microscope for the first time ever, overcoming numerous technical challenges relating to the performance and stability of the electron microscope itself. The microscope can measure the electromagnetic fields inside a material at the atomic level. It is anticipated that the microscope will assist in the development of new functional materials by uncovering the mechanisms that determine the performance of materials such as those used in magnets, battery electrodes, and superconductors.

Global Collaboration with CEOS of Germany and CEMES of France

Hitachi is engaged in collaboration with partner businesses and research institutions on the development of solutions and equipment. One example is a project to incorporate a spherical accelerating corrector into a large TEM with high acceleration voltage in partnership with Corrected Electron Optical Systems GmbH (CEOS) of Germany.

Spherical aberrations in the electron lenses used in electron microscopes are an obstacle to improving resolution. CEOS successfully developed a spherical aberration corrector in the mid-1990s. However, to get the best performance from the corrector, the electron microscope in which it is installed must have a high level of stability. Hitachi, Ltd. and Hitachi High-Technologies have been working with CEOS on a joint project to incorporate this spherical aberration corrector into TEMs since 2003. To date, the project has succeeded in installing the corrector in a 200-kV scanning transmission electron microscope [STEM(i)] and a 300-kV TEM. In the case of the atomic-resolution holography electron microscope, the installation of the spherical aberration corrector in the large, ultra-high-voltage (1.2-MV) TEM helped achieve world-leading resolution. Engaging in collaborative creation not only means working together to take on the challenges of technical innovation, it also results in close contact between the people involved. This issue of *Hitachi Review* includes an article contributed by Prof. Dr. Max Haider, who led the development of the spherical aberration corrector, that gives an overview of the joint development by CEOS and Hitachi.

In collaboration with the Center for Materials Elaboration and Structural Studies (CEMES), an institute of the French National Center for Scientific Research, Hitachi also developed and delivered an electron microscope with world-class resolution by installing an aberration corrector in a 300-kV TEM. CEMES uses TEMs for the research and development of magnetic materials for use in permanent magnets for hybrid vehicles or hard disk drive (HDD) heads. While electron microscopes use a magnetic field to

* The development process, instrument characteristics, future applications, and other details about the atomic-resolution holography electron microscope are described in reference 1) (*Hitachi Review* 64, Nov. 2015).

(i) STEM
Scanning transmission electron microscope. A type of TEM, an STEM scans a tightly focused electron beam over the sample (like an SEM) and uses a detector located under the sample to detect the transmitted electron beam and form an image. STEMs are used in applications such as observing grain boundaries in materials made up of crystals of different types.

CEMES: Center for Materials Elaboration and Structural Studies
FE-TEM: field-emission transmission electron microscope

Fig. 2—FE-TEM with Spherical Aberration Corrector.
The microscope was developed and supplied in collaboration with CEMES, an institute of the French National Center for Scientific Research. CEMES is recognized as a leading European laboratory for materials science and is well known for the high level of its technology for electron microscopes. I2TEM can perform both interference fringe observation and atomic-level kinetic observation (in situ observation), and so it was named I2TEM in reference to the two initial i's of interference and in situ. An inscription reading '愛²TEM' (愛 is pronounced 'I' and means 'love') was added to the main body to commemorate the passion of the project participants.

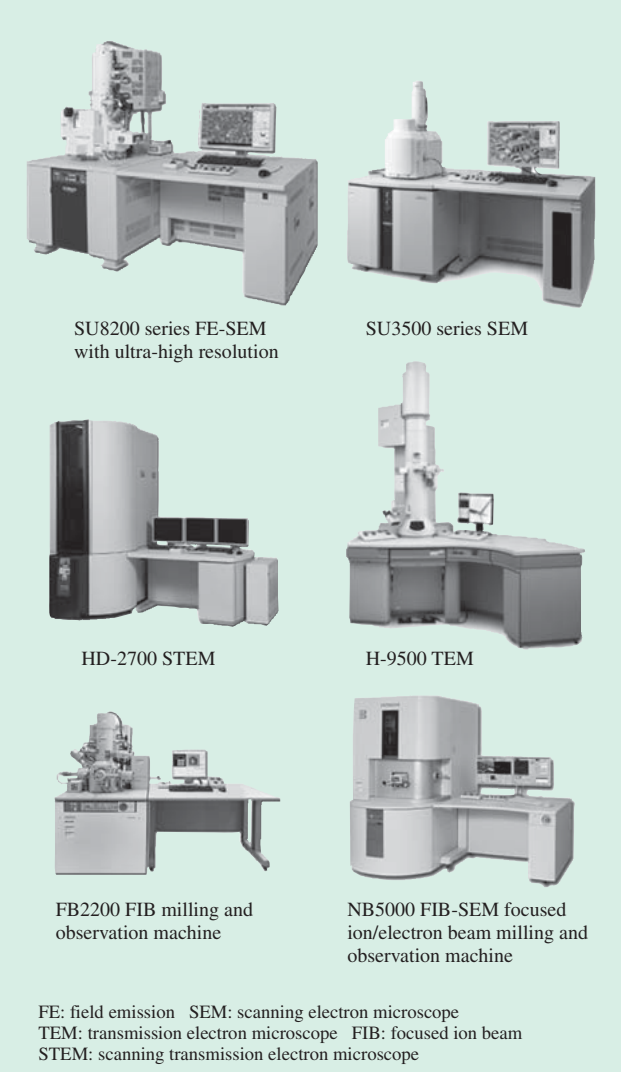


Fig. 3—Electron Microscope and FIB Milling and Observation Machine.
Hitachi High-Technologies has a full product range that extends from models with high resolution and performance to general-purpose models. FE microscopes achieve high resolution by using an FE electron source, a technology that Hitachi High-Technologies was the first in the world to commercialize.

control the electrons, there was a strong need for high-resolution observation of magnetic materials in an environment free of magnetic fields (where the sample is not influenced by the magnetic field used for electron beam control). A high-resolution field-emission transmission electron microscope (FE-TEM) fitted with a field emission (FE) electron gun able to achieve high resolution was used as the base instrument, and the CEOS spherical aberration corrector was installed to further improve the resolution (see Fig. 2). As a result, the instrument achieved a spatial resolution of 0.5 nm in the targeted region that was free of magnetic fields. It is seen as having potential future uses that include improving the performance of permanent magnets for hybrid vehicles or achieving higher densities and read speeds on HDDs. Potential uses are also being sought in cancer treatment and other medical applications.

Satisfying Leading-edge Requirements for Electron Microscopes and FIBs

Hitachi High-Technologies has an extensive range of electron microscopes and focused ion beam (FIB[j]) products, including TEMs, SEMs, FE-SEMs, STEMs, and FIBs (see Fig. 3). The development and supply

(j) FIB
Focused ion beam. FIB systems are used to perform milling on the surface of a sample by scanning a very tightly focused ion beam over it, or to acquire microscope images of the exterior material by detecting the secondary electrons that are emitted as a result. They have the same design and functions as an SEM except that whereas an SEM uses an electron beam, an FIB system works by directing a beam of gallium or noble gas ions at the sample. Because these ions are much more massive than electrons, they cause spattering by expelling atoms from the sample. This effect can also be used for etching the sample to perform milling to expose a cross section for observation, and for the preparation of TEM samples by extracting a thin fragment from a particular location on the sample.

of functions and other solutions to meet leading-edge requirements for these instruments is ongoing, including improvements to resolution and other aspects of performance.

One of these leading-edge requirements is for in situ observation ("operand measurement"), meaning the observation of materials in actual use. There is strong demand for studying things like catalyst reaction mechanisms and what is happening inside lithium-ion batteries or fuel cells. In response, Hitachi High-Technologies has developed an environmental control mechanism. This uses an atmospherically isolated sample holder to prevent the sample from coming into contact with the air and is equipped with functions such as heating or gas injection. It is used for in situ observation using a variety of measurement and analysis techniques, and is supplied as a system that can be used in conjunction with an SEM, TEM, or SPM, or with sample preparation systems such as for FIB milling (see Fig. 4).

Another leading-edge requirement is for three-dimensional analysis, meaning the three-dimensional imaging and analysis of things like material composition and the internal structure of devices. To satisfy this demand, Hitachi High-Technologies has developed a realtime three-dimensional analytical combined FIB and SEM instrument (see Fig. 5). This provides an easy way to build up a three-dimensional image of the internal structure of a sample by progressively milling small quantities of material and performing automatic imaging. It achieves high resolution by using an SEM to perform the imaging during FIB milling. The three-dimensional analysis of things like composition and crystal orientation that are essential to the study of materials is also made possible by fitting additional instruments such as an X-ray analyzer or electron backscattering diffraction analyzer.

COLLABORATION WITH KEY OPINION LEADERS

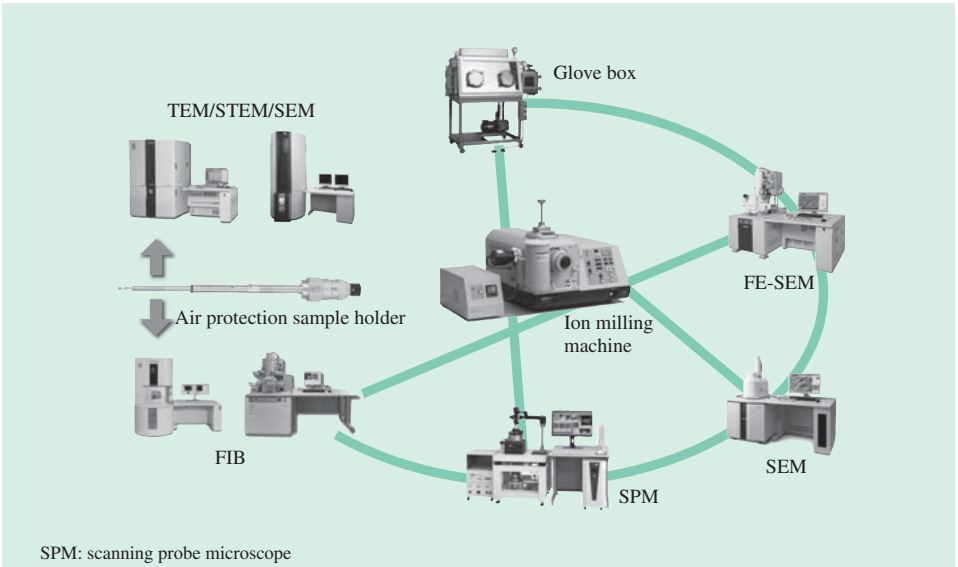
To satisfy these leading-edge requirements, Hitachi is actively pursuing collaboration with key opinion leaders at universities and other research institutions in Japan and elsewhere to create new technologies and other solutions.

This issue of *Hitachi Review* carries articles contributed by leaders in the deployment of the leading-edge measurement and analysis techniques to research and development covering the latest research findings and example applications, and describing work on the development of new solutions being undertaken in partnership with Hitachi.

Application to Fuel Cell Research Using Controlled-environment SEM/STEM In Situ Observation

In situ observation of catalysts and other functional materials and three-dimensional analysis of their microstructure are being used in the development of new materials for environmental and new energy fields.

Professor Akari Hayashi of Kyushu University is researching fuel cell catalysts for the use of hydrogen energy. She had a strong need for a way to perform realtime observations of surface reactions on fuel



SPM: scanning probe microscope

Fig. 4—Linkage System with Air Protection Sample Holder. The sample holder is designed to prevent exposure of the sample to the atmosphere and is also equipped with functions for things like heating or gas injection. The same holder can be used in electron microscopes, SPMs, and sample preparation machines. The system combines the different types of measurements, and performs in situ measurement of samples under the conditions in which they are used in practice ("operand measurement").

Fig. 5—NX9000 Realtime Three-dimensional Analytical FIB-SEM. The NX9000 can analyze the three-dimensional structure of microscopic regions by building up a series of consecutive cross section images through an automatic process of repeated FIB section milling and SEM observation. The three-dimensional analysis of things like material composition and crystal orientation is also possible by fitting additional instruments such as an X-ray analyzer or electron backscattering diffraction analyzer.

cell electrode catalysts under the conditions (such as atmosphere and temperature) in which the catalysts are used. The environmental control mechanism described above (see Fig. 4) was a good match for these requirements. She used the environmental control mechanism to set up an experimental laboratory for catalyst surface reactions inside an SEM or STEM and undertook in situ observations. In addition to nanoscale observations of degradation mechanisms and what changes occur under the conditions in which catalysts are used, the technique was also used to assess catalyst life.

Three-dimensional Microstructure Analysis of Materials Using Orthogonally-arranged FIB-SEM

There is growing demand in the development of new materials for three-dimensional analysis to obtain more detailed information on the internal structures of samples. It was against this background that Hitachi worked with Dr. Toru Hara, Group Leader, the National Institute for Materials Science (NIMS), to develop a realtime three-dimensional analytical combined FIB and SEM instrument (see Fig. 5) and observation techniques for using the new instrument. The instrument is used to perform detailed observation of metals, ceramics, and other materials through its ability to build up and analyze three-dimensional images by automating FIB milling and SEM observation and analysis.

Use of High-resolution SEM/STEM for Structural Analysis of Materials with Regular Porous Structure

Assistant Professor Toshiyuki Yokoi of the Tokyo Institute of Technology focuses his research in the field of resource and catalytic chemistry on zeolites, a class of high-performance catalysts that are environmentally conscious. Zeolites are microporous crystalline minerals that contain voids of uniform size at the molecular scale (0.3 to 1 nm). One of the problems with the structural analysis of zeolites under a high-resolution SEM or STEM is that the electron beam causes changes in the shape of the sample. However, by achieving higher resolution at a low acceleration voltage, the technology is contributing to the development of zeolite catalysts by making it possible to image the shape of the zeolite surface on the order of a few nanometers.

Applications in Biology and Medicine, and iPS Cell Research

Electron microscopes have been used in biology and medicine for such tasks as making structural observations of microscopic viruses, cells, and biological samples since they were first developed.

Professor Akira Sawaguchi of the University of Miyazaki has put a lot of effort into promoting the use of electron microscopes in biomedical applications, instructing young medical researchers on the importance of observing microscopic features. Meanwhile, making practical use of induced pluripotent stem (iPS) cells requires techniques for verifying their quality, and Professor Akira Sawaguchi has sought to use electron microscopy for this purpose. The professor is contributing to the study of iPS cells by enabling realtime observation with a link between a laboratory in Kyoto and the University of Miyazaki to monitor the day-by-day growth of iPS cells.

Realtime Stereo SEM for Three-dimensional Imaging of Structure of Biological Samples

Many of the biological functions of organisms have yet to be elucidated and there is a high level of demand for ways of making detailed observations of biological samples. Practice to date has been to perform dissections and observe them under an optical microscope. However, because of the limits on the observation of microscopic structures, Professor Tatsuo Ushiki of Niigata University wished to build a system that would allow dissections to be performed while viewing three-dimensional images under an SEM.

Accordingly, Hitachi High-Technologies, Niigata University, Shizuoka University, and Eizo Nanao Corporation (now EIZO Corporation) jointly participated in a Japan Science and Technology Agency (JST) program for the development of advanced measurement and analytical techniques and equipment and succeeded in implementing an SEM capable of realtime three-dimensional imaging and a high-resolution monitor for viewing the images with the naked eye. The system has been incorporated into a commercially available SEM and is used for structural observations in a variety of fields, including materials development as well as biology.

In addition to the initiatives described here, Hitachi is also participating in open innovation and collaborative creation with universities and research institutions in Japan and elsewhere involving a large number of different measurement and analysis techniques, not only electron microscopy. In the future, Hitachi intends to continue to work on the development of measurement and analysis techniques that satisfy leading-edge requirements by drawing on a global network of advanced research.

CREATING INNOVATIONS AND BREAKTHROUGH TECHNOLOGIES, DEVELOPING NEW MARKETS

In addition to creating revolutionary innovations and breakthrough technologies for measurement and analysis through the development of proprietary technologies, Hitachi is also working to expand the scope of measurement and analysis techniques.

Tabletop Electron Microscope for Observation under Atmospheric Pressure

Normally, observation using electron microscopes is done in a vacuum to prevent scattering of the electron beam due to collisions with molecules in the atmosphere. However, because water-containing samples such as biological materials are subject to evaporation in a vacuum, it has been difficult to view them in their raw state. Moreover, it was believed that obtaining SEM images at atmospheric pressure was impractical because electron beam scattering has a large effect under these conditions. For the newly developed AE1500 atmospheric-pressure tabletop electron microscope (see Fig. 6), Hitachi High-Technologies went back to the principles behind electron beam scattering to consider how to build the instrument and succeeded in obtaining crisp SEM images under atmospheric pressure by developing a correction technique that removes the influence of the scattered electron beam from the SEM image. In the future, the technology is expected to find uses in applications such as food, cosmetics, pharmaceuticals, and medicine where SEMs have not been widely used in the past.

Fig. 6—AE1500 Atmospheric-pressure Tabletop Electron Microscope.
Hitachi High-Technologies built an atmospheric-pressure SEM featuring simple sample setting by challenging the common-sense view that obtaining SEM images at atmospheric pressure was impractical due to scattering of the electron beam. Water-containing samples such as biological material can be viewed in their raw state without the water evaporating. The technology is expected to find new uses in applications such as food, cosmetics, pharmaceuticals, and medicine.

Development of New Markets Using Tabletop Electron Microscope

The TM series were the first tabletop electron microscopes to go on the market (see Fig. 7). Past electron microscopes have been expensive devices used by skilled operators. The TM series of tabletop microscopes are designed to be as easy to use as an optical microscope while still providing the resolution of an electron microscope, combining tabletop installation with simple and easy operation. They have been adopted at industrial workplaces where electron microscopes have not been used in the past. As part of its corporate social responsibility activities, Hitachi High-Technologies also uses the TM series to support science education throughout the world.

FIB-based Photomask Repair System

While FIB machines have diverse uses, Hitachi has developed a technique for repairing defects on photomasks and implemented it in the form of an FIB system specifically for use in semiconductor device manufacturing (see Fig. 8). In place of a liquid metal ion source of the type used to generate

Fig. 7—TM3030 Tabletop Microscope.
The TM3030 is a tabletop electron microscope that is easy to use, with minimal restrictions on where it can be installed. With its ability to be fitted with a cooling stage for samples and an (optional) X-ray analyzer for composition analysis, the microscope is opening up new markets such as manufacturing plants. Users include natural history museums and science museums as well as elementary schools, junior high schools, and other educational institutions.

Fig. 8—Photomask Defect Repair System Using FIB.
The system is used to view defects on semiconductor photomasks and repair them using micro-fabrication technologies such as etching or deposition. The same system can be used for imaging, material removal and deposition using an FIB.

ion beams for the past 30 years or more, Hitachi has made a breakthrough in miniaturization technology by developing a novel gas field ion source. Hitachi has achieved the minimum process dimension, optical, and other characteristics required for photomask repair by improving the resolution of scanning ion microscope images(k), and has demonstrated its use for repairing defects in photomasks or extreme ultraviolet (EUV) masks for the latest microelectronic devices.

PROVIDING SOLUTIONS IN DIVERSE FIELDS FROM ANALYSIS AND OBSERVATION TO MEASUREMENT

To perform accurate analyses efficiently in response to diverse needs, it is useful to combine a variety of different analysis techniques. Hitachi High-Technologies has been consolidating its analyzer business in Hitachi High-Tech Science. Hitachi High-Technologies intends to supply solutions to a wide variety of fields by further developing its technologies for SPM, optical measurement, ion optics, mass spectrometry, thermal analysis, and X-ray and other techniques for non-destructive testing, and by integrating measurement and analysis equipment.

(k) Scanning ion microscope image
An image generated by detecting the secondary electrons discharged when a sample is scanned with an focused ion beam (FIB). This provides better composition and crystal orientation contrast than an SEM image. The instrument that obtains the images is called a scanning ion microscope (SIM).

Fig. 9—AFM5500M SPM.
The AFM5500M simultaneously images the three-dimensional profile of a sample and maps its physical properties at the nano level by scanning its surface with a needle-sharp probe. Applications range from nano-scale research and development to industrial measurement applications such as quality management.

SPMs

SPMs can measure the surface profile of a sample or its mechanical, electrical, and other properties with high (sub-nanometer) resolution. They are suitable for making precise measurements over microscopic regions of several hundred micrometers or less. With excellent resolution in both the horizontal and vertical directions, they can perform height and other shape measurements with nanometer precision. In response to demand from industrial measurement applications, the latest SPMs (see Fig. 9) are capable of making high-quality measurements, with simple

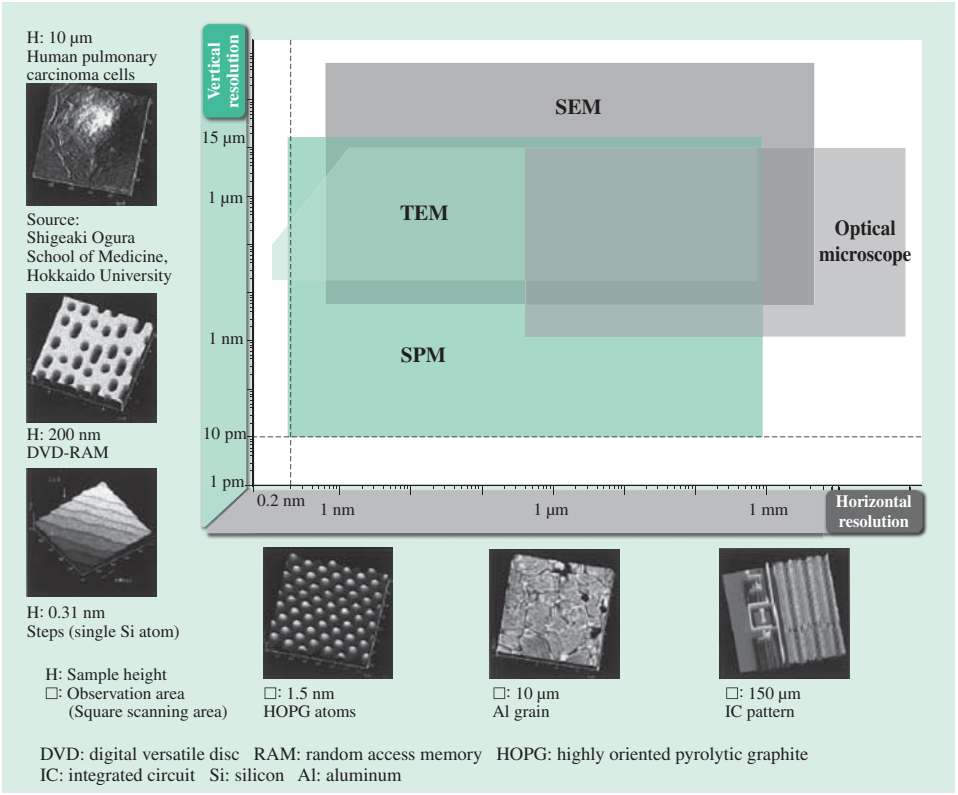


Fig. 10—Comparison of Resolutions of Different Types of Microscopes.
SPMs have excellent vertical resolution and can also measure physical properties. SPMs can be used to complement SEMs and TEMs.

operations that do not depend on the skills of the operator, thanks to improved three-dimensional shape measurement precision and improved ease-of-use through measurement automation.

Hitachi High-Tech Science has also developed a controlled-environment SPM unit that can be used to perform analyses under a variety of conditions, including in vacuum or in solution. This unit can be used to perform electrical measurements under ultra-high vacuum in a way that minimizes the influence of water adsorbed by the sample surface, and to map the properties of the sample under heating or cooling conditions. By taking advantage of these capabilities, applications for SPMs are expanding from nano-scale research and development to industrial measurement and quality control.

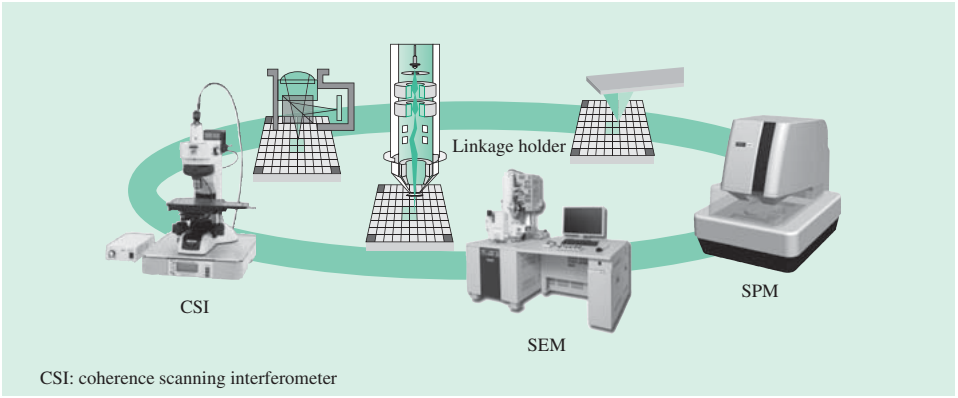
Microscope Linkage System

As noted above, SPMs can perform height and other shape measurements, three-dimensional length measurements, and physical properties measurements with nanometer precision over microscopic regions of several hundred micrometers or less. SEMs, by contrast, can obtain surface profile images over a wide area more quickly than SPMs. This means that SPMs and SEMs complement each other (see Fig. 10). Accordingly, the two different types of microscopes can be used together to perform complementary observations and measurements in ways that take advantage of their respective strengths.

Hitachi High-Technologies Group has developed a technique for observing the same location using a number of different microscopes by providing a shared alignment sample holder and a coordinate linkage function for SEMs, SPMs, and the coherence scanning interferometers (CSIs) described below (see Fig. 11). It is possible, for example, to measure the same location using an SEM and SPM and combine the information from the two microscopes for evaluation. This leads to the creation of new observation solutions, with one example application being a study of a lithium-ion battery that combines the contrast of an SEM with SPM surface potential observations (see Fig. 12) to display both its internal structure and the electromagnetic properties at the same location. Hitachi High-Tech Group intends to supply comprehensive solutions that use this linkage system to make it easy to integrate observation, analysis, and measurement by a number of different methods.

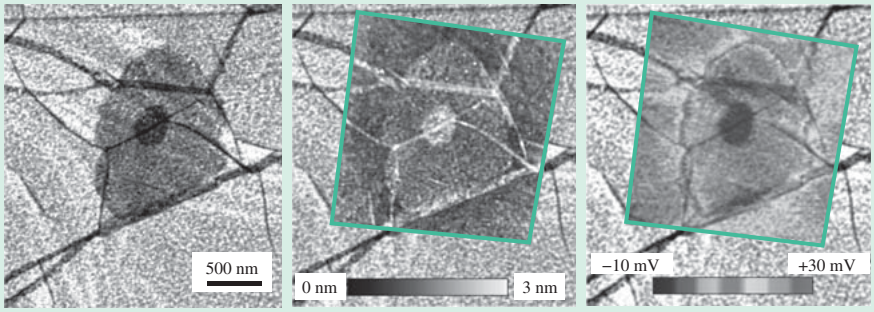
Coherence Scanning Interferometer (CSI)

CSIs use optical interference to perform rapid measurements of surface profile over a wide area or things like the thickness of multi-layer transparent



CSI: coherence scanning interferometer

Fig. 11—Microscope Linkage System.
This system provides a simple way to observe the same sample location on a number of different microscopes (SPM, SEM, and CSI) by using a shared alignment sample holder and a coordinate linkage function.



CVD: chemical vapor deposition SiO_2: silicon dioxide

Fig. 12—Example of SEM-SPM Linkage Application.
The images show graphene grown by CVD on SiO_2. They are obtained by overlaying shape and electrical potential images acquired for the same location by an SEM and an SPM. The contrast in the SEM image comes from the SPM images of shape and surface potential.

film (see Fig. 13). They take only a few seconds to make surface profile measurements with high vertical resolution of 0.01 nm over a wide area (several millimeters). They also provide a non-contact and non-destructive way to measure the film thickness or layer cross section of multi-layer transparent film, or to detect the presence of contaminants, peeling, or other defects. A coordinate linkage function is also available for integration with an SEM or SPM. It is anticipated that the scope of applications will expand in the future to include things like control of surface roughness over wide areas or in inspection devices in the film production process.

Food Analysis Technology Driven by Fluorescence Fingerprints

The food industry has a close relationship to people's daily lives and there is growing demand for things like the identification of origin and type or composition analysis for reasons of food safety. Hitachi High-Tech Science has developed an analytical technique based on spectroscopy that uses the fluorescence fingerprints of food samples (the pattern of wavelengths, intensities, and other properties of fluorescent light) (see Fig. 14). This provides a simple and low-cost way to analyze the identity of samples and so on by efficiently acquiring large quantities of fluorescence fingerprint data using a high-speed scanning fluorescence spectrophotometer and subjecting it to statistical analysis to obtain a small number of distinctive indicators. This has been made possible by advances in information technology

Fig. 13—CSI VS1000 Series.
An optical interference technique is used to achieve both a wide field of view and high vertical resolution (two attributes that in the past were believed difficult to achieve at the same time). This takes advantage of the properties of light to combine non-contact surface profile measurement and layer cross-section measurement.

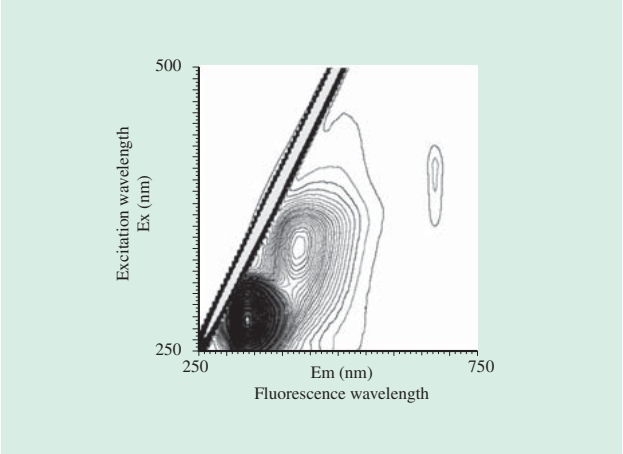


Fig. 14—Fluorescence Fingerprint Example (Pineapple Juice). Fluorescence fingerprinting treats the fluorescence pattern obtained from factors such as the wavelength and intensity of fluorescent light like a human fingerprint. This meets demand for things like the identification of origin and type or composition analysis due to rising concern about food safety and security.

(IT) and information processing. There is interest in using the technology in the food industry, and Hitachi High-Tech Science intends to work on application development with research institutions and other partners.

Compact Mass Detector for HPLC

In the drug development and manufacturing sectors, there is growing demand for uses such as research into chemical synthesis or production management where structural and quantitative analyses are performed and composition analysis using liquid chromatography (LC)/mass spectrometry (MS) systems that combine a mass spectrometer with high performance liquid chromatograph [HPLC(l)]. By making the system significantly smaller and more compact with easier operation and maintenance through the development of the Chromaster 5610 compact mass detector (see Fig. 15), Hitachi High-Tech Science has overcome concerns about the installation requirements for previous large mass spectrometers and about their operation and maintenance and made it possible for HPLC users to enjoy the high level of qualitative analysis performance that is characteristic of a mass spectrometer. This issue of *Hitachi Review* describes three applications from the drug development sector [the analysis of the intermediate products of synthesis by direct infusion, the screening of microorganism culture fluid by LC/MS, and the analysis of a mixture by thin-layer chromatography-mass spectrometry (TLC-MS)]. In the future, Hitachi High-Tech Science intends to proceed with the development of applications that will expand uses for mass spectrometers by taking advantage of its simplicity.

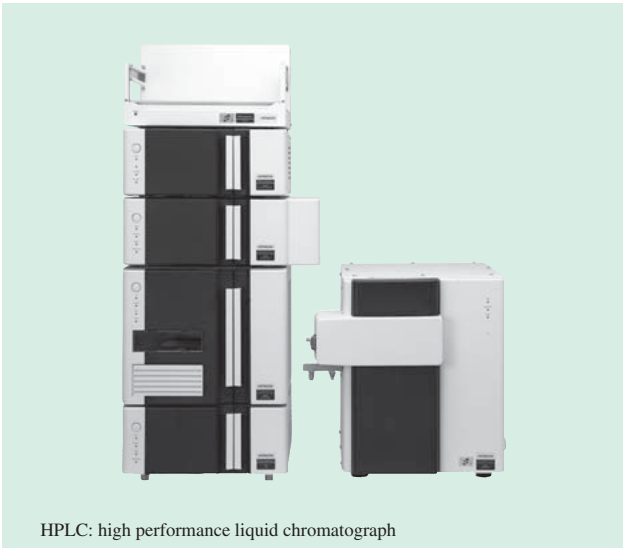
(l) HPLC
High-performance liquid chromatograph. A chromatograph is a device for separating a mixture into its component parts and recovering (isolation or refinement) or quantifying them. A liquid chromatograph is used to perform measurements on liquid samples, or on solids that have been dissolved in a solvent.

Fluorescent X-ray Technique for Coating Thickness Measurement and Particle Contaminant Analysis

As it seeks to achieve smaller size and higher performance, the control of things like defects or particle contaminants that have an influence on quality is an important issue for the electronics sector, including semiconductors and other electronic components or lithium-ion rechargeable batteries. The sector uses non-destructive techniques such as X-ray fluorescence (XRF).

XRF analysis uses the secondary (fluorescent) X-rays emitted by a sample when it is exposed to incident X-rays to perform quantitative analysis and to identify the elements present in a sample. The technique is characterized by its speed and by its being non-destructive.

Coatings and platings are used on the electronic components, circuit boards, connectors, and other



HPLC: high performance liquid chromatograph

Fig. 15—Compact Mass Detector for HPLC. Hitachi High-Tech Science supplies systems that are easy for a large number of users to operate in fields such as drug development by incorporating a compact Chromaster 5610 mass detector (right) into a Chromaster HPLC system (left).

XRF: X-ray fluorescence

Fig. 16—FT150 Series High-performance Fluorescent X-ray Coating Thickness Gauge.
The FT150 series gauge performs fast non-contact measurement of the thickness of the coatings (platings) used on electronic components for smartphones and other devices. It satisfies quality control requirements at leading-edge production facilities by providing a specific-purpose gauge based on XRF analysis.

items used in devices such as smartphones, and there is growing demand for ways to measure coating (plating) thickness. Hitachi High-Tech Science has utilized the characteristics of XRF analysis to commercialize techniques for exposing small areas to X-rays and the highly sensitive detection of X-rays in the form of a coating thickness measurement system (see Fig. 16). On production lines for electronic components used in smartphones and other devices, the system is helping ensure the durability of electrical connections involving the pins and other connectors on electronic components by being able to deal with plating thicknesses at the nanometer level over areas several tens of micrometers in size.

Meanwhile, the use of lithium-ion rechargeable batteries and fuel cells is growing in a variety of fields as a way to reduce the load on the environment. Management of contamination by metal particles in the production process is important for ensuring the safety and quality of these cells. Hitachi High-Tech Science has developed an X-ray particle contaminant analyzer that combines particle detection by transmitted X-ray imaging with element identification by XRF analysis in the same system (see Fig. 17). The system helps improve cell yield and operating life by dealing with small metal particles of around 20 μm in manufacturing process for products such as lithium-ion rechargeable batteries and fuel cells.

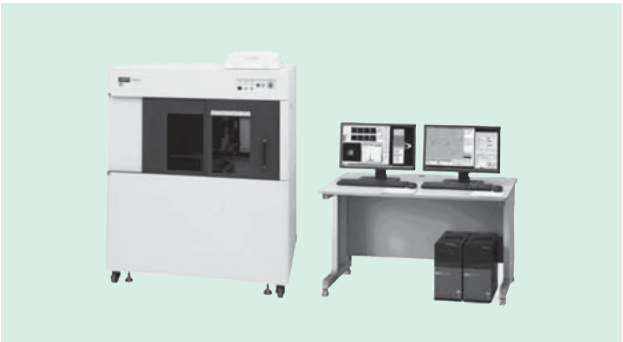


Fig. 17—X-Ray Particle Contaminant Analyzer EA8000.
The EA8000 is used to ensure the safety and quality of lithium-ion rechargeable batteries and fuel cells by dealing with contamination by metal particles in the production process. It operates quickly and efficiently, with functions that extend from the detection of metal particles to the analysis of their composition.

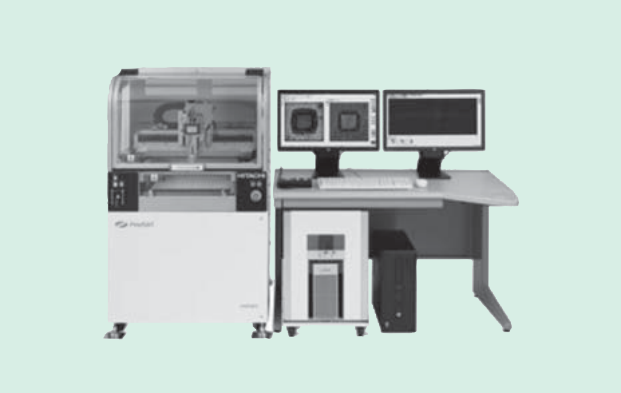


Fig. 18—Scanning Acoustic Tomograph (SAT).
The SAT machine uses ultrasound to perform non-destructive detection of cracks, delamination, and voids in electronic components. In response to demand for higher resolution and greater miniaturization, the instrument utilizes a focused ultrasound beam and image restoration to image small defects of between 1 and 1.6 μm, which are difficult to detect using conventional technology.

Non-destructive Defect Inspection Using Ultrasonic Imaging

Along with X-rays, ultrasonic imaging is another widely used technique for the fast and non-destructive detection of defects and similar in materials, with marked improvements having been made in things like resolution and detection speed. On the latest scanning acoustic tomograph (SAT) machine commercialized by Hitachi Power Solutions Co., Ltd. (see Fig. 18), the ability to detect microscopic internal defects has been improved to between 1 and 1.6 μm, more than twice the performance of previous models, by using the resolution-enhancing technology and image restoration technology to enable use with smaller semiconductors and other electronic devices. This is helping make semiconductors and electronic devices more reliable through the imaging of microscopic defects that were difficult to detect on past machines.

DEVELOPMENT OF INNOVATIVE TECHNOLOGY AND STRENGTHENING OF TECHNOLOGY PLATFORMS

Research & Development Group, Hitachi Ltd. is responsible for the development of innovative technology for measurement and analysis and the strengthening of technology platforms. The group works in parallel with product development at Hitachi, systematizing technology platforms and different fields of technology so as to strengthen and collate specific technologies that support fundamental product characteristics such as performance and reliability[(2)].

In addition to contributing to quality improvement and reliability in manufacturing at Hitachi, the purpose of the inspection and measurement technology platform for manufacturing is to provide an impetus to the inspection and measurement equipment business. Four core technologies have been selected: (1) visible inspection and measurement, (2) non-destructive inspection, (3) chemical measurement and probe imaging, and (4) optical 3D shape measurement. Hitachi is working on the development of leading-edge technologies that include techniques for the precise detection of external and internal defects and the imaging or identification of conditions or situations that are not yet evident.

In the case of the charged particle control platform for the electronics sector, Hitachi is developing measurement and processing techniques that use charged particles such as electrons and plasma neutrons or photons such as X-rays, synchrotron radiation, or laser light. In the application of electron beams to measurement, Hitachi is developing instruments such as measurement SEMs for the critical dimension measurement of semiconductor devices using an electron gun and electron optics with excellent stability and resolution. In the case of plasma control, Hitachi is using the creation and control of plasmas and the analysis of surface reactions to develop nanometer-level microfabrication techniques for semiconductors. In the case of measurements that use high-energy quantum beams such as X-rays or synchrotron radiation, Hitachi is utilizing high-intensity beam lines to develop measurement techniques for functional materials such as the computed tomography (CT) imaging of composites or chemical bonds, or in the case of the non-invasive optical measurement of biological samples using infra-red and other low-energy radiation, is utilizing things like Raman scattering of infra-red laser light to develop cell measurement techniques that do not require staining for use in regenerative medicine or drug development.

CONTRIBUTING TO SCIENCE AND SOCIETY THROUGH WORK ON ADVANCES IN MEASUREMENT AND ANALYSIS TECHNOLOGIES

Measurement and analysis technologies are used everywhere from research and development to quality management, supporting progress in science and the safety and security of society. Hitachi intends to make an ongoing contribution to the development of new technologies and solutions that bring about social innovations by continually striving to make further progress in measurement and analysis technologies and supplying the best solutions for the measurement and analysis requirements of different fields.

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Special Contributions

Development of Aberration Correctors for the HD-2700, the HF3300S, the 1.2 MV FIRST Program, and Future Prospects

Prof. Dr. Max. Haider
Dr. Heiko Müller

EDITOR'S SUMMARY: For electron microscopes, the spherical aberration of the electron lenses has long been an obstacle in the way of improving resolution. Finally, in the mid-1990s, a system for correcting spherical aberration was developed. However, there were many technical challenges for implementing it in a high voltage STEM/TEM. In coope-ration with CEOS GmbH which had been developing a spherical aberration corrector (Cs-corrector) for practical use, Hitachi, Ltd. and Hitachi High-Technologies Corpo-ration developed a 200 kV STEM and a 300 kV TEM that implement spherical aberration correctors, and achieved a significant improvement in resolution. In addition, the companies succeeded in incorporating a Cs-corrector into a 1.2 MV atomic-resolution holography electron microscope. This made a great contribution to achieving world-leading resolution.
In the development of these instruments, in addition to the development of spherical aberration correctors that support high-voltage and ultra-high-voltage, the electron microscope itself required a significant improvement in stability. Through close cooperation, the companies have solved these technical issues one by one. In this paper, Prof. Dr. Max. Haider, who founded CEOS and has led the development of spherical aberration correctors, summarizes the development CEOS carried out in cooperation with Hitachi, Ltd. and Hitachi High-Technologies Corporation.

INTRODUCTION

THE successful implementation of a Cs-corrector first for a high resolution 200-kV transmission electron microscope (TEM)[(1)] and later on also for the scanning transmission electron microscope (STEM) has stimulated the development of a new generation of high-resolution TEM and STEM instruments. With the research prototypes of the Cs-correctors it became quite clear that the previously existing microscopes were simply not prepared to provide sufficient stability in electronics and mechanics to allow for routine atomic-resolution imaging. In this paper we summarize the efforts and development we carried out in cooperation with Hitachi, Ltd. and Hitachi High-Technologies Corporation in order to provide novel aberration-corrected instruments. After first discussions at the Microscopy & Microanalysis meeting 2003 in Quebec/Canada we initially concentrated on the development of a hexapole-type probe corrector for Hitachi's dedicated STEM HD-2700. Almost thirty systems of this type have been installed since then. Later, with the availability of Hitachi's new 300-kV high-resolution (S)TEM HF3300S, equipped with a cold field-emission gun (C-FEG), we continued with the development of a three-hexapole imaging-corrector with large field of view and dedicated capabilities for field-free (Lorentz) imaging. Just recently we supplied an imaging corrector for the 1.2 MV atomic-resolution holography electron microscope within the framework of Tonomura's FIRST program. Together with Hitachi and Hitachi High-Technologies our next step now is to equip the HF3300S instrument with an advanced hexapole-type probe corrector in order to fully exploit the high-resolution and analytic capabilities of this 300-kV C-FEG instrument.

PROBE CORRECTOR FOR A 200-kV DEDICATED STEM

The hexapole-type Cs-corrector as proposed by Rose as a theoretical concept[(2)] at first has been successfully

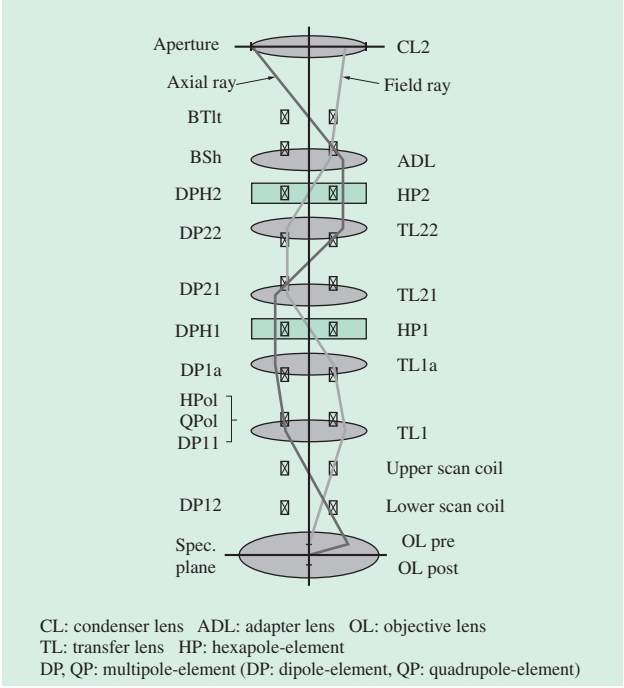

Fig. 1—Schematic Drawing of a Hexapole-corrector for STEM. This corrector has two transfer lenses (TL1, TL1a) between the objective lens (OL) and the first hexapole-element (HP1) and a 2nd transfer-lens doublet (TL21, TL22) between the two hexapole-elements (HP1, HP2). With additional weak multipole-elements (DP, QP) the required precise ray-path and focus planes can be aligned. The dark gray ray shows the axial ray and the light gray ray the field ray.

employed as an imaging corrector in a 200-kV TEM[1]. This corrector (see Fig. 1) is based on two strong hexapole elements which generate magnetic fields with three-fold symmetry. The first hexapole field produces a strong threefold astigmatism which has to be compensated by the second hexapole field. This can be achieved by placing two round lenses in between the two hexapole elements. Additionally, the correction unit must be matched optically with the objective lens in a proper way. This again is done by additional round lenses between the objective lens and the correction unit. The production and compensation of the strong three-fold astigmatism by long hexapole elements placed at two optically conjugated planes generates - as a secondary effect - a negative third-order spherical aberration. This effect is used to compensate for the spherical aberration of the objective lens. A very similar design can be used in a probe-forming system too. Fig. 1 shows a sketch of a hexapole-type Cs-corrector for STEM. The simplicity of this design is the basis of its success over the last few years. The primary benefit of Cs-correction in TEM is to enable proper phase-contrast without artifacts from spatial delocalisation or phase reversal up to the information limit of the instrument. For STEM the most important parameter is the usable aperture size and the available total current in the probe-forming system. A Cs-corrector allows the probe semi-angle to be greatly increased while the probe size is maintained or even reduced. In this case resolution is not limited by diffraction anymore but by the brightness of the electron source. Achievable probe profiles and probe diameters are illustrated in Fig. 2. Besides the brightness, the energy width of the gun is also an important parameter for

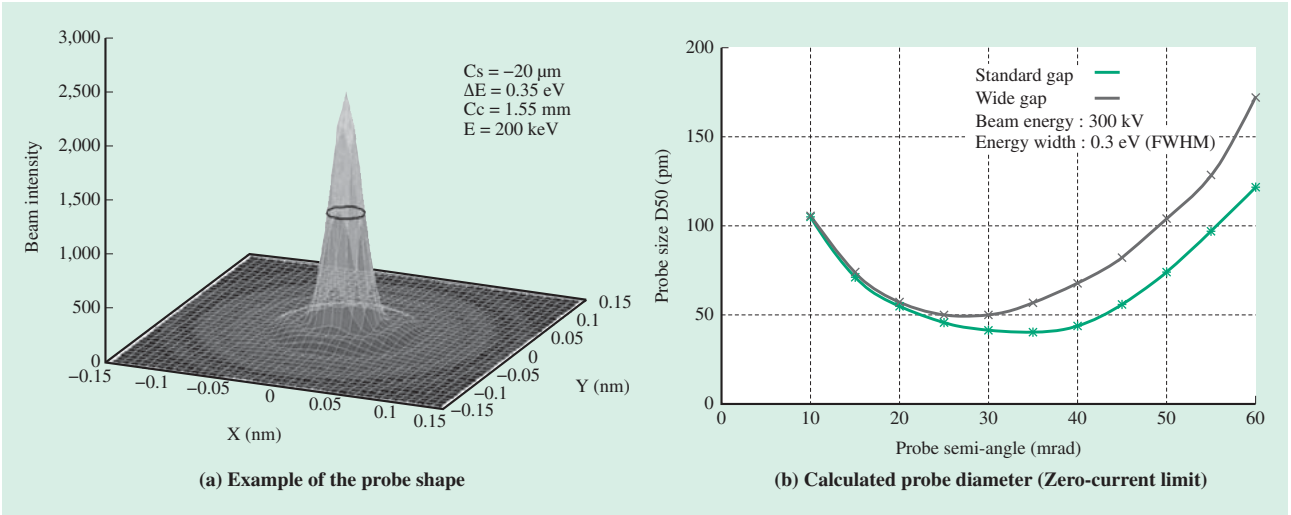

Fig. 2—Example of the Probe Shape and Calculated Probe Diameter.
In (a), as an example, the probe shape is given for a 200 kV electron probe. The small ring indicates the FWHM. On (b), the calculated probe diameter is given for various illumination angles. One easily can observe the influence of the chromatic aberration and the energy width of the electron probe on the probe diameter.

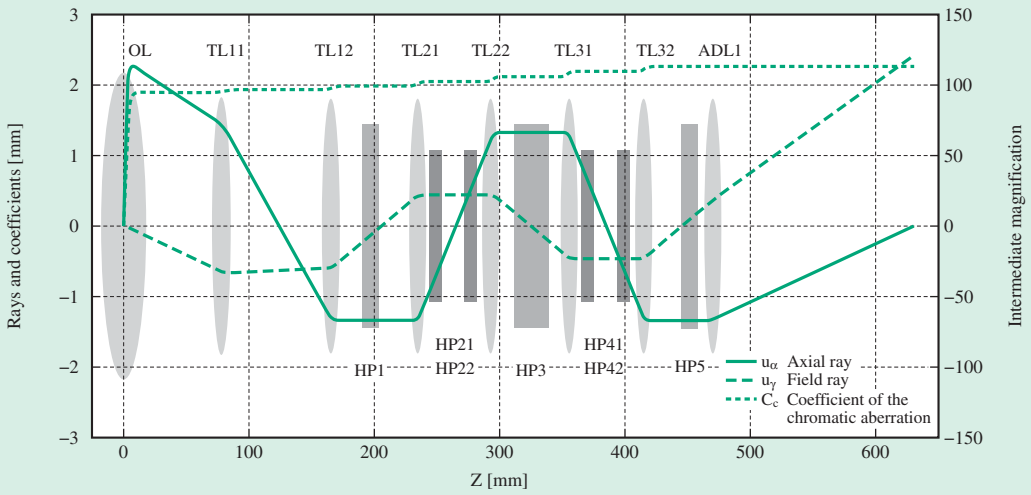

Fig. 3—Beam Path for the B-COR Design from the Objective Lens (OL) to the First Intermediate Image Plane below the Corrector. The axial ray uα, the field ray uγ, and the coefficient of the chromatic aberration Cc are plotted. The light-gray boxes indicate the strong hexapole triplet HP1/HP3/HP5 and the dark-gray boxes show the position of the anti-symmetric weak hexapole doublets HP21/HP22 and HP41/HP42. Additionally, all seven transfer lenses are shown. The given intermediate magnification value shows the increase of the field of view with respect to the object plane at various intermediate planes within the correction system.

the sharpness of the electron probe especially when working at energies below 80 kV. Therefore, Hitachi's HD-2700 equipped with a C-FEG that has a small intrinsic energy width provides a good platform for sub-Angstrom resolution with analytic capabilities[3]. Even by detecting the signal from secondary electrons (SE), atomic resolution could be demonstrated[4].

APLANATIC IMAGING CORRECTOR FOR A 300-kV TEM

A TEM equipped with a two-hexapole imaging Cs-corrector by design is semi-aplanatic. For a fully aplanatic system, the remaining off-axial aberrations of the objective lens also have to be compensated and the parasitic off-axial aberrations must be controlled. This can increase the number of equally-well resolved image points from a few hundred to some thousand image points. The most critical off-axial aberrations are the off-axial coma and the variation of the two-fold astigmatism across the field of view. A three-hexapole design can be used to compensate for all axial aberrations up to fifth order including the six-fold astigmatism and for all off-axial aberrations up to third order[5, 6]. A schematic drawing of such an aplanatic corrector is depicted in Fig. 3. This novel design has been implemented successfully as an imaging corrector for the HF3300S TEM. It allows for aberration-free imaging for an effective imaging aperture of 30 mrad or larger (see Fig. 4). At 300 kV an information limit better than 70 pm could be demonstrated[7]. As an important feature, the corrector allows easy tuning of the relevant axial aberrations and the lower-order off-axial aberrations including the azimuthal off-axial coma. Fig. 5 illustrates the effect of parasitic off-axial astigmatism before and after correction. This improvement helps to guarantee

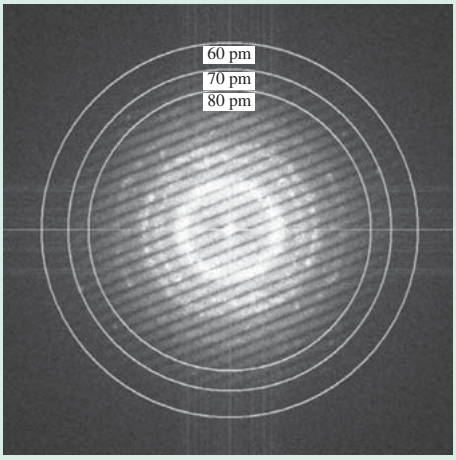

Fig. 4—Central Region of a Young's Fringe Pattern from a Thin Tungsten Specimen.
A Young's fringe pattern is recorded at 300 kV with 4 s illumination time. The Nyquist frequency in the original image is 38.3 nm^{-1}. The fringe pattern spreads outside of 70 pm.

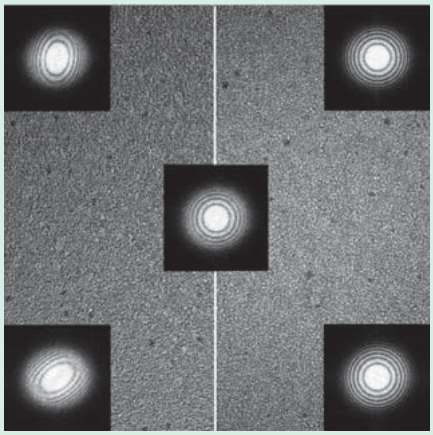

Fig. 5—Comparison Before/After Off-axial 2-fold Astigmatism A_{1G} Correction.
An amorphous Tungsten foil has been imaged at 60 kV with a field of view of 70 nm. The left side (a) shows the residual phase shift due to an off-axial 2-fold astigmatism in the diffractograms at the left corners and at the right hand side (b) the compensation of this off-axial astigmatism is demonstrated by the diffractograms at these positions. The phase shift by this aberration is much smaller and almost not visible by eye.

a large field of view for aberration-free imaging even with a 4k x 4k or 8k x 8k camera. This feature makes the system particularly attractive for holography and large field-of-view applications. Optionally, for the HF3300S, the corrector can be used for Cs-corrected field-free (Lorentz) imaging with the specimen placed at the upper stage or at the objective lens stage position. An example is given in Fig. 6 which was provided by the group of E. Snoeck at CEMES/Toulouse. All holography options of the HF3300S are supported by the corrector too.

ADVANCED PROBE CORRECTOR DCOR

The Hitachi Cold-FEG provides a high spectral brightness. In STEM this allows for a large probe semi-angle since the effects from the chromatic aberration of the probe-forming system are reduced. With the classical design of the hexapole corrector in this case, limitations have to be expected due to its intrinsic six-fold astigmatism and uncompensated parasitic fourth-order aberrations. This provided the motivation for an advanced design of the hexapole-type probe corrector. By incremental changes, we could eliminate the effects of the six-fold astigmatism and add means to correct for all parasitic fourth-order axial aberrations. This has been achieved by using an optimum length and excitation of the two hexapole elements and by exploiting a combination aberration of the hexapole fields with the transfer lenses in between[8]. Just recently, this design has been implemented for Hitachi's HF3300S[9]. The aim is to allow for considerably larger probe semi-angles and accordingly larger probe currents for analytic work at atomic resolution. The system is designed to enable deep sub-Ångstrøm resolution with wide-gap type pole pieces and Cs-corrected STEM imaging with the specimen placed at the upper stage in field-free (Lorentz) mode. Both are very attractive for modern in-situ and lab-in-the-gap applications. This probe corrector also helps to improve the quality of the illumination system in TEM and fully supports holography with a double bi-prism in the condenser system for split-beam illumination.

IMAGING Cs-CORRECTOR FOR A 1.2 MV HOLOGRAPHY ELECTRON MICROSCOPE

The late Akira Tonomura, who passed away much too early in 2012, initiated the FIRST program for which he received funding from the Japanese government. His idea was to combine the world's most advanced techniques to achieve an unprecedented resolution in transmission electron microscopy. However, the highest resolution was not only meant to resolve the

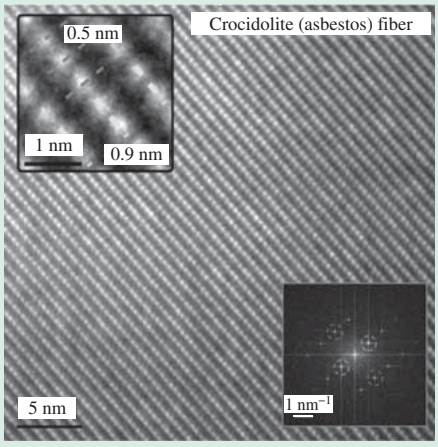

Fig. 6—Imaging of Crocidolite with this Object in a Field Free Area (Lorentz Mode).
The small insets show an enlarged view of the smaller object area (top left corner) and the diffractogram (lower right corner) indicating the achieved resolution. In the diffraction pattern one can see reflections out to about 5 Å (courtesy of C. Gatel & E. Snoeck, CEMES-CNRS, Toulouse France).

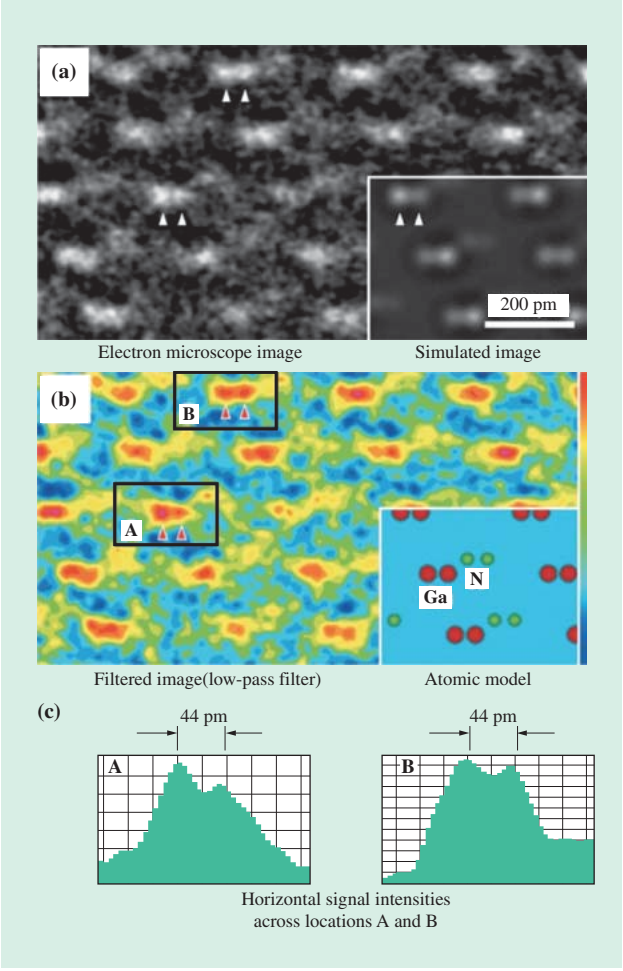

Fig. 7—Imaging of Ga Atom Spacing in GaN.
(a) shows a high-resolution TEM image of a GaN [411] thin sample. Projected Ga atom positions (white arrows) with 44 pm separation were clearly observed. (b) shows the corresponding Gaussian low-pass filtered image. The color key on the right shows the image intensity. (c) shows the line profiles of the Ga atom pairs indicated by black rectangles A and B in (b). Ga atom pairs were also clearly resolved in these profiles. [from T. Akashi et al., Appl. Phys Let. 106 (7), 074101, 2015].

smallest details, he also wanted to measure phase shifts of electrons by electromagnetic fields with atomic resolution, a so far unavailable precision. For this goal he started the development of a new high voltage TEM equipped with a cold field emitter – for highest coherence – and decided to use a Cs-corrector to avoid delocalisation of information due to the spherical aberration of the objective lens. Due to the extremely high beam energy and the size of the instrument, the development of the Cs-corrector has been a true challenge.

It employed the standard two-hexapole design, but the necessary strength, power dissipation and possible magnetic saturation effects of all optical elements had to be considered very carefully. After a theoretical feasibility study and detailed design, the manufacturing could finally be started. A critical point was that the proper function of the corrector and also the correctness of the underlying theory could only be tested very late in the final stage of the implementation. Due to the excellent cooperation between Hitachi and CEOS, this project was finished successfully without any delay caused by the corrector technology.

The initially anticipated resolving power of the system finally could be demonstrated for high-resolution imaging and in Cs-corrected Lorentz mode for field-free imaging. Here, a new technique has been used with an extra dedicated Lorentz lens in between the upper stage and the objective lens. As shown in Fig. 7 the achievable resolution is at least 44 pm and the adjacent Gallium columns in GaN <114> are clearly resolved[10]. This currently is considered a new world record in TEM resolution. The FIRST program microscope is now in operation and used for holography and other precision measurements.

Today, the long-lasting, fruitful and successful cooperation between Hitachi and Hitachi High-Technologies in Japan and CEOS in Germany is looked back on with gratitude. Not only in terms of technological challenges, but also at the personal level, the relationship between the companies became very close. During more than one decade together the companies were able to successfully finalize four challenging development projects, one further project currently is a work in progress and some other ideas are expected to become reality in the future.

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Special Contributions

Studies on Degradation Mechanism of Electrocatalysts for Fuel Cells through In-situ SEM/STEM Observation

Akari Hayashi, Ph.D.

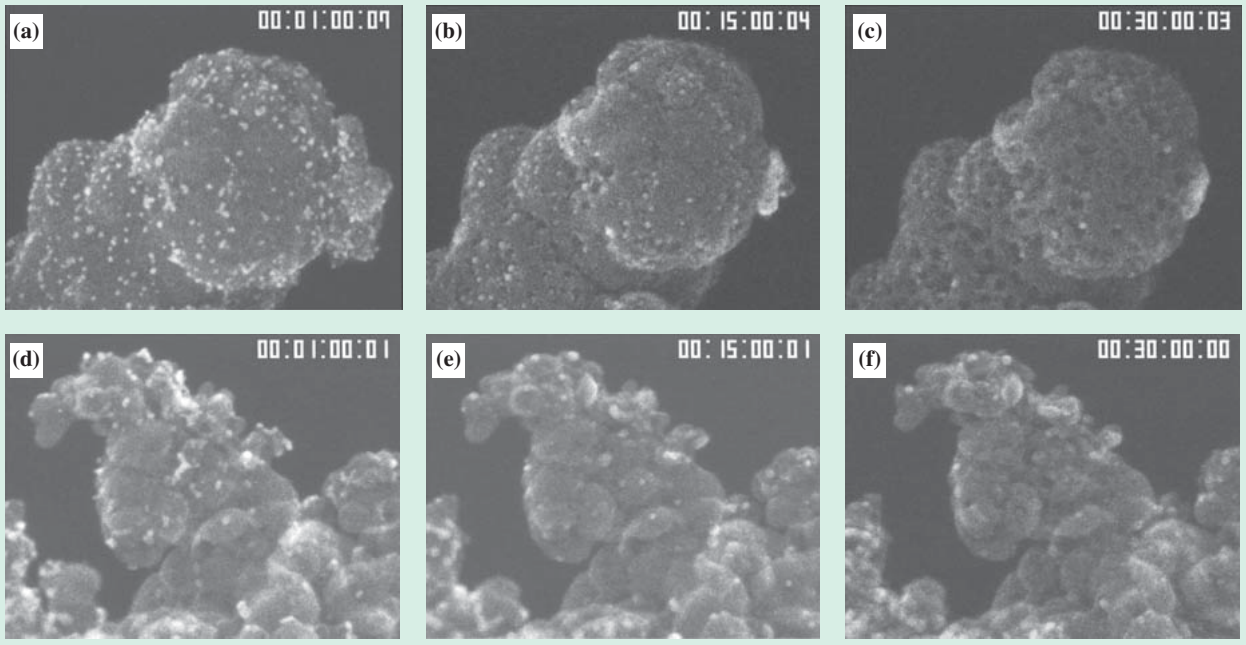
OVERVIEW: Electrode catalysts play a crucial role as the key determinant of the performance of fuel cells, a technology recognized as being central to the wider adoption of hydrogen-based energy. Electrode catalysts are composed of platinum nanoparticles distributed on a carbon support, and this carbon is known to degrade at high voltage due to oxidation. This article describes a technique for assessing catalyst durability through in-situ observation under an SEM/STEM in a controlled atmosphere. The technique introduces air to create an oxidizing atmosphere and performs in-situ observation of the degradation process. Simultaneous SEM/STEM observation identified the sinking of platinum particles due to carbon oxidization as one of the degradation mechanisms. This direct observation of this degradation process will provide a valuable analytical technique for the future design of materials with high durability.

INTRODUCTION

POLYMER electrolyte fuel cells (PEFC) are recognized for their potential as a core technology for the wider adoption of hydrogen-based energy. Having first come onto the market in 2009 for stationary applications, PEFCs have also been commercially available for use in fuel cell vehicles since December 2014. However, mainstream adoption of fuel cells will also require rapid improvements in performance, durability, and cost. Among the constituent materials in fuel cells, electrode catalysts are a crucial element with the greatest influence on cell performance, and typically, these employee materials in which platinum nanoparticles are supported on a carbon support. The platinum catalyst degradation that occurs during starting, stopping, and idling is a known major factor in cell deterioration. Particularly during starting, cathodic potential rises to a peak value of approximately 1.5 V, which corrodes (oxidizes) the carbon support[1]. In conjunction, platinum-carbon support interactions decrease, causing phenomena such as particle growth in the platinum catalyst and loss or dissolution from the support, and degrading the electrode catalyst. In this context, recent research has re-examined catalysts, supports, and catalyst-support interactions to offer new, corrosion-resistant materials which improve fuel cell durability. Our research group has succeeded in improving electrode catalyst durability by applying a heat treatment to a carbon support to form a graphite surface and controlling its degree of graphitization[2].

Techniques for evaluating electrode catalyst performance include “half-cell” techniques evaluating only the cathodic side of a cell, and fabrication of membrane electrode assemblies (MEAs) to evaluate fuel cells in cell units. In either case, durability is generally evaluated according to electric potential cycle protocols proposed by the Fuel Cell Commercialization Conference of Japan[1, 3]. For example, in an electric potential cycle protocol simulating automobile starting and stopping, cycling between 1.0 and 1.5 V is repeated at the rate of 1 cycle every 2 seconds. Repetition of 60,000 cycles allows evaluation of durability over approximately 20 years. This is a useful evaluation protocol which can also be implemented in ordinary university research laboratories. However, while the protocol allows detailed evaluation of, for example, degradation every 10,000 cycles, 2 to 3 days per sample elapse before 60,000 cycles are completed; and moreover, it is difficult to study issues bearing on an understanding of degradation mechanisms, such as nanoscale structural change during cycling.

Consequently, in cooperation with the Matsumoto group at Hitachi High-Technologies Corporation, we



SEM: scanning electron microscope Pt: platinum VC: VULCAN carbon GVC: graphitized VULCAN carbon

Fig. 1—In-situ SEM Observation.
The photographs show Pt/VC (a) 1 min., (b) 15 min., and (c) 30 min. after air introduction, and Pt/GVC1600 (d) 1 min., (e) 15 min., and (f) 30 min. after air introduction.

experimented with a new technique[4] for evaluating electrode catalyst durability a short time frame of 30 minutes through use of an accelerated degradation testing protocol entailing heating of electrode catalyst specimens in an atmospheric air environment, and simultaneous, in-situ scanning electron microscope/scanning transmission electron microscope (SEM/STEM) observation.

EXPERIMENTAL PARAMETERS

Our research used TEM/STEM equipped with SEM functionality and an air supply system developed for in-situ TEM use to perform in-situ observation of the behavior of platinum nanoparticles on carbon in an atmospheric environment. Simultaneous in-situ SEM/STEM observation was carried out for 30 minutes with air introduced near the observed specimen and a specimen heating temperature of 200°C. The specimens used for observation were platinum/VULCAN*1 carbon (VC) produced by a method[5] using commercial VULCAN XC72 and a platinum acetylacetonate precursor. For comparison, platinum/graphitized VULCAN carbon 1600 (GVC1600) carrying platinum was used in an analogous method following heat treatment of VULCAN XC72 at 1,600°C to graphitize the surface. The amount of platinum carried was approximately 20% in each samples. A previous report[2] states that, among both samples, durability was improved in platinum/GVC1600 with a graphitized surface after evaluation by the electric potential cycle protocol described above. In addition to these two samples, a platinum/Ketjen Black (KB: commercial Ketjenblack*2 EC-600JD) catalyst carrying platinum in similar fashion was used in ex-situ SEM/STEM observation. Platinum/KB, a sample demonstrating very low durability in electric potential cycle testing, was evaluated for comparison to platinum/VC and platinum/GVC1600.

IN-SITU SEM/STEM OBSERVATION

Fig. 1 shows SEM images at 1, 15, and 30 minutes after introduction of air to platinum/VC and platinum/GVC1600 specimens. As shown in Fig. 1 (a), approximately 2 nm of platinum particles was found

*1 VULCAN is a registered trademark of Cabot Corporation.

*2 Ketjenblack is a registered trademark of Akzo Nobel Chemicals B.V.

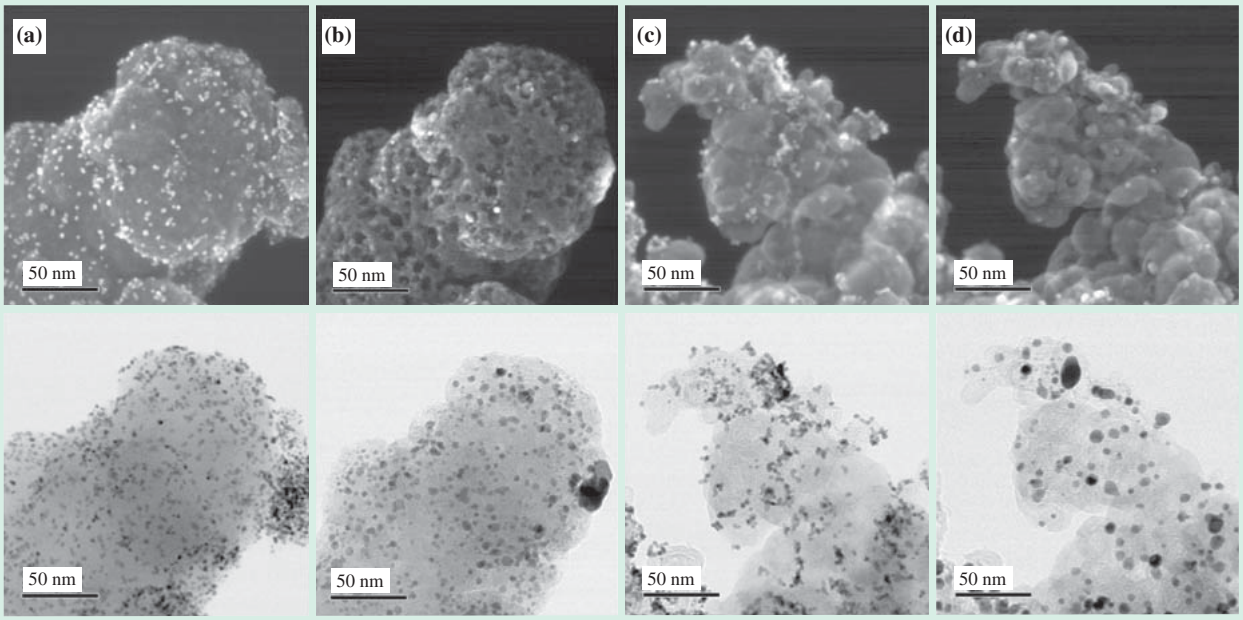


Fig. 2—Simultaneous In-situ SEM/STEM Observation.
The photographs show Pt/VC after (a) 1 min. and (b) 30 min., and Pt/GVC1600 after (c) 1 min. and (d) 30 min.

to be distributed uniformly on the carbon support surface in the initial platinum/VC. After introduction of air, virtually no movement of platinum particles on the carbon support was observed, and likewise, virtually no associated aggregation or coarsening. As seen from the SEM image after 15 minutes shown in Fig. 1 (b), the process of platinum particle penetration to the interior of the carbon support was observed actively. Thereafter, the shape of the carbon support was maintained, but as reaction time proceeded, the surface structure changed into a porous form, and after 30 minutes, as shown in Fig. 1 (c), nearly all of the platinum particles were found to have sunk into the support interior. As seen from the simultaneous SEM/STEM observation images shown in Fig. 2 (a), in early stages, both images show nearly identical platinum particles, indicating that platinum particles were present only on the surface of the carbon support. However, major differences in the SEM and STEM images are seen in Fig. 2 (b) 30 minutes after observation, and simultaneous observation with SEM showed that degradation of the catalyst not apparent from the STEM image alone was caused by a decrease in active sites, the major reason for which was the phenomenon of particle sinking, rather than particle growth.

In the GVC1600 specimen, similarly, dispersion soon after air introduction in Fig. 1 (d) was somewhat worse than in the platinum/VC specimen, with particles of approximately 2–3 nm supported on the carbon support. However, as air was introduced, as shown in Fig. 1 (e), the platinum/GVC1600 specimen demonstrated aggregation and coarsening of platinum particles in conjunction with their movement on the carbon support surface, a phenomenon virtually unobserved in the platinum/VC specimen. At such time, no apparent sinking of platinum particles into the support was observed. Thereafter, as reaction time proceeded, some sinking of platinum particles into the support was observed, but as shown in the SEM image in Fig. 1 (f) after 30 minutes, the sinking of platinum was largely suppressed. Then, as shown in the simultaneous SEM and STEM observation images in Fig. 2 (c) and (d), initially and after 30 minutes, respectively, no major difference was seen in the state of platinum dispersion, another indication that sinking of platinum particles into the support was largely suppressed.

Our research discovered that aggregation, dissolution, and loss, the previously conceived mechanisms of platinum degradation, are also augmented by a new mechanism of platinum

degradation[4], specifically, corrosion of the carbon support surface by platinum particles, with sinking of particles into the support, and substantial reduction in the platinum-active surface. While it has become apparent that graphitization of a carbon surface suppresses carbon corrosion and improves durability by previous evaluations based on electric potential cycle protocols, improved durability was also confirmed by our new technique.

EX-SITU SEM/STEM OBSERVATION[6]

The new degradation mechanism of platinum particle sinking is important to PEFC research for its consistency with actual degradation mechanisms occurring in PEFC. For this reason, we carried out simultaneous ex-situ SEM/STEM observation of degraded Pt/VC and Pt/GVC1600 through electric potential cycling protocols. Fig. 3 (a) and (b) present the results for Pt/VC, and Fig. 3 (c) and (d) present the results for Pt/GVC1600. In all samples, there was no observed discrepancy in Pt dispersion in SEM versus STEM images, and the phenomenon of platinum sinking was not confirmed.

We therefore performed simultaneous ex-situ SEM/STEM observation of platinum/KB specimens, which have very low durability in electric potential cycle testing, after such testing. As shown in Fig. 4 (a) and (b), platinum particles seen in STEM images were not seen in SEM images, and SEM images confirmed

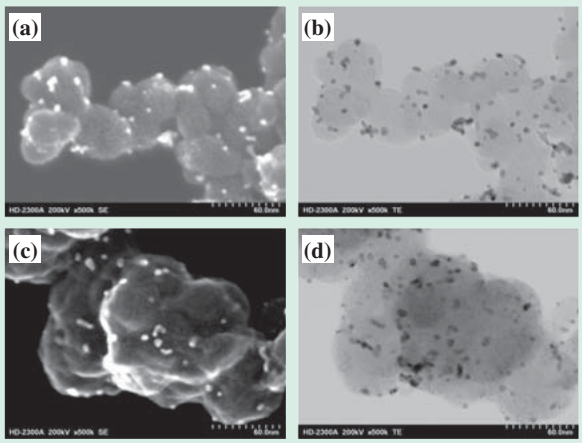
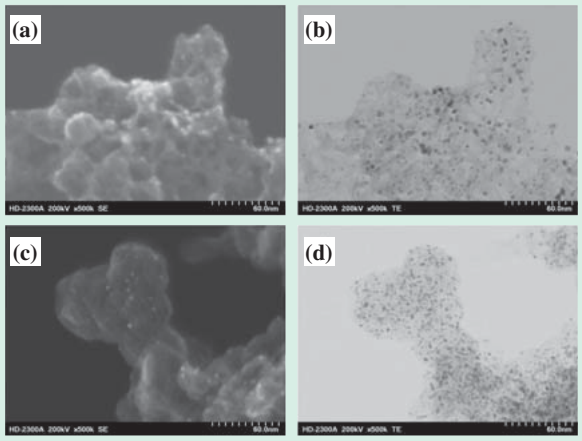


Fig. 3—Simultaneous Ex-situ SEM/STEM Observation of Pt/VC and Pt/GVC1600.
The photographs show (a) SEM and (b) STEM images of Pt/VC, and (c) SEM and (d) STEM images of Pt/GVC1600 after electric potential cycle degradation testing (60,000 cycles).



KB: Ketjenblack

Fig. 4—Simultaneous Ex-situ SEM/STEM Observation of Pt/KB. The photographs show (a) SEM and (b) STEM images after, and (c) SEM and (d) STEM images before electric potential cycle degradation testing (60,000 cycles).

the presence of holes opened on the surface of the support, suggesting, in other words, that carbon surface corrosion opened holes, and platinum particles sank. Here we note that comparison of platinum/KB SEM/STEM images before electric potential cycle testing did not show as many platinum particles in SEM images as were seen in STEM images, due to the hollow structure of KB, and this comparison did not confirm the presence of holes opened in the carbon surface. From this fact, we understand that one degradation mechanism entails degradation of carbon by application of electric potential cycling, formation of holes, and sinking of platinum particles into the carbon.

In sum, we have concluded that an accelerated degradation testing protocol involving heating of an electrode catalyst material in an environment of atmospheric air presents accelerated degradation conditions more severe than those in electric potential cycle testing, but similar mechanisms cause degradation.

CLOSING REMARKS

Through an in-situ SEM/STEM simultaneous observation protocol, we confirmed that the accelerated degradation testing protocol used in our research, wherein an electrode catalyst material is heated in an atmospheric air environment, allowed evaluation of electrode catalyst durability in a short time frame. The evaluation results were also consistent with patterns in

results to date for electric potential cycle testing. We believe that this protocol will prove to be an extremely important analytical technique in fuel cell research, and we hope that its adoption will extend beyond observation of electrode catalysts to observation of catalyst layers including ionomers, thereby furthering fuel cell research.

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Special Contributions

Microstructure Analysis by Means of the Orthogonally-arranged FIB-SEM

Toru Hara, Dr. Eng.

OVERVIEW: Serial sectioning using a combined FIB and SEM is a method for three-dimensional imaging of material microstructures. Hitachi set out to achieve precise three-dimensional imaging of material microstructures with higher spatial resolution and contrast than previous instruments by utilizing a configuration in which the FIB and SEM are positioned orthogonally (perpendicularly), this being the ideal orientation for three-dimensional imaging. This manuscript gives an overview of an FIB-SEM with an orthogonal configuration intended for three-dimensional imaging, describes the multi-functionality and high-performance imaging that are features of the instrument, presents examples of its use, and considers future developments.

INTRODUCTION

THE basis of structural observation in either light microscopy or electron microscopy is essentially recording of two-dimensional images, either through surface observations produced by reflection, or through projected observations produced by transmission. However, apart from a very small category of exceptions, the structure of materials and biological object is by nature three-dimensional. Consequently, innovative means have long been employed to allow three-dimensional observations.

For specimens such as the metals and ceramics that we study, microstructural observation is required over a wide range of scales from the subnanometer level to the micrometer and millimeter level. In this context, three-dimensional reconstructed image observation with serial sectioning using a hybrid "focused ion beam-scanning electron microscope" (FIB-SEM) is of interest for the comparatively broad coverage that it provides.

Here we provide an overview of a perpendicularly-oriented FIB-SEM (SMF-1000, Hitachi High-Tech Science Corporation) that we adopted to provide highly precise three-dimensional observations of materials structures. We also describe practical examples of its use in observation. We adopted this instrument in February 2011, and since then, the equipment and related observational technologies have proliferated widely as "Multi-Scale Analytical Equipment for Three-Dimensional Microstructures" under the Nanotechnology Platform initiative of the Ministry of Education, Culture, Sports, Science and Technology (MEXT). We also present some practical examples of observation under these initiatives in various research fields.

INSTRUMENTATION AND ITS TECHNIQUES[1]

Serial sectioning by an FIB-SEM unit combining FIB and SEM functions in one unit has been used widely to date. In this technique, the surface layer of a specimen is ground by FIB, the ground layer is observed repeatedly by SEM, and the series of SEM images acquired is integrated by computer to reconstruct a three-dimensional image. As a result, the quality of the SEM image depends greatly on the quality of observation and analytical results. One issue to note during serial sectioning observation by FIB-SEM is the fact that even though this is nominally an SEM observation, it is observation of a surface which has been cut by FIB, not a morphological observation revealing surface irregularities. In other words, the external form of the specimen is not observed. An almost perfectly flat surface is created, and contrast within its internal structure is observed by secondary electrons or reflected electrons. Consequently, the contrast observed results from the type and density of constituent elements of the specimen, and in the case of crystalline specimens, its structure or channeling (orientation), and the technique is essentially inapplicable for topographic contrast. The type of contrast to be used for a desired observation is a parameter (detector and detection parameters) which must be investigated.

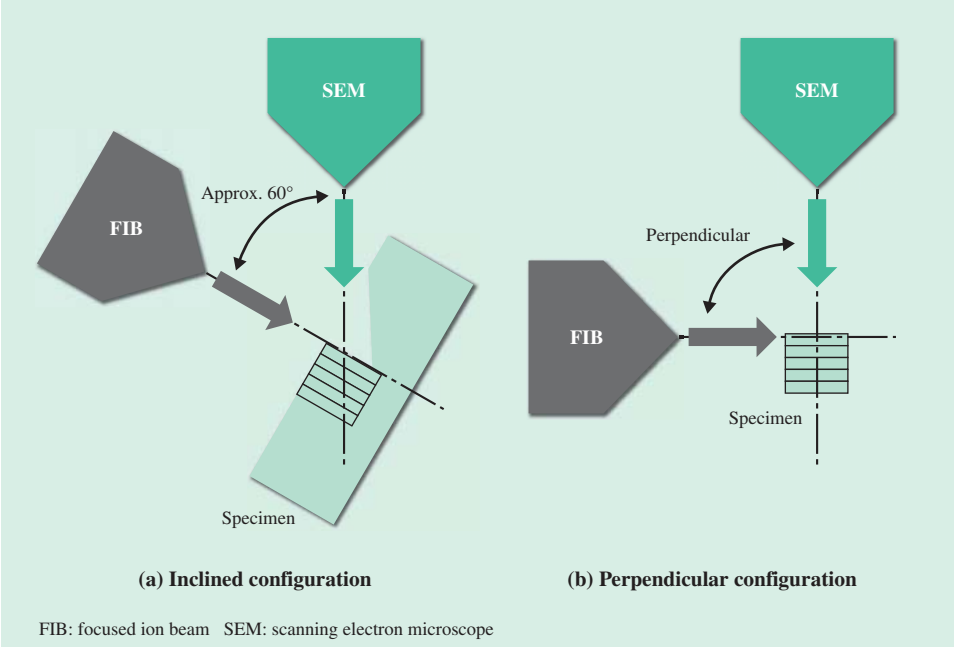

Fig. 1—Configuration of FIB and SEM in FIB-SEM.
(a) shows how the FIB and FEM are oriented at an angle of about 60° to each other on a conventional FIB-SEM. This orientation is not ideal for three-dimensional imaging because the FIB cutting surface is not perpendicular to the optical axis of the SEM. (b) shows how, on the orthogonally-arranged FIB-SEM, the FIB cutting surface is perpendicular to the optical axis of the SEM, thereby enabling undistorted observation of the surface and eliminating field of view misalignment.

To date, general FIB-SEM instrument has been employed for this purpose; specifically, as shown in Fig. 1 (a), instrument in which the optical axes of FIB and SEM units intersect each other at a roughly 60° angle. This is the best configuration for FIB and SEM to visualize the same point and is ideally suited, for example, for SEM location of a site and FIB preparation and removal of a sample for TEM observation. However, if the objective is limited to serial sectioning observation, this configuration is not necessarily ideal for the following two reasons:

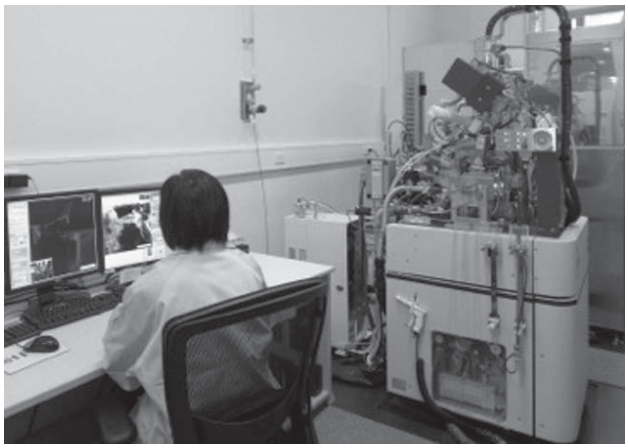

Fig. 2—External Appearance of the Orthogonally-arranged FIB-SEM Apparatus.
The FIB is located on the left side of the SEM, which is positioned above the instrument on the right of the photograph. The specimen is inserted from the front side, as viewed in the photograph.

(1) As shown in Fig. 1 (a), repeated slicing by FIB causes field of view misalignment in an SEM image. Because the area cut is offset from the center of the SEM image (dotted line in the figure), correction is required.
(2) The SEM optical axis is not perpendicular to the FIB sliced plane. This results in SEM observation of an inclined surface, and for example, when attempting observation using a secondary electron image, most of the dynamic range in contrast is consumed by phenomena arising from high/low differences. Additionally, because an inclined plane is observed, the vertical and horizontal scales even within the same SEM image differ and require correction.

For these reasons, an ideal equipment configuration for the purpose of serial sectioning has the FIB cutting surface perpendicular to the SEM optical axis, as shown in Fig. 1 (b).

To achieve this end, we introduced an observational instrument configured with the FIB and SEM elements perpendicular to each other (SMF-1000, Hitachi High-Tech Science Corporation). Fig. 2 shows a photograph of the instrument as it appears. This instrument creates no changes in contrast due to high/low differences on the cutting surface, a configuration ideally suited to internal structural observation. Additionally, to collect as much information as possible in a single observation, the instrument is provided with an energy dispersive X-ray spectrometer (EDS), an electron backscatter diffraction (EBSD) detector, and specimen preparation equipment such as a plasma cleaner, argon

ion gun, and gas deposition gun. The image detectors provided are an SEM in-lens type secondary electron detector and an in-lens reflected electron detector (i.e., one located coaxially on the optical axis of SEM microscope tube), and an Everhart-Thornley (E-T) detector, as well as a scanning transmission electron microscope image (STEM) detector immediately below the specimen.

APPLICATION EXAMPLES FOR MICROSTRUCTURE OBSERVATION

Two-dimensional Image Observation of Clean Surface

Before discussing an example of three-dimensional reconstructed image observation, we touch on the fact that the quality of ordinary two-dimensional images (SEM) per se is high. While the internal microstructure sometimes cannot be seen from the specimen surface due to issues such as surface layers or oxide layer, the cutting in FIB allows observation of a fresh surface without such impediments. For example, Fig. 3 shows a specimen of a steel material with a surface finished to smoothness by electropolishing. A surface oxide layer has been formed during electropolishing, and rather than contrast in the internal structure, all that can be observed is irregularities in the surface oxide layer. This is shown on the left half of Fig. 3. The right half of the figure shows the specimen with its surface oxide layer removed by FIB (located at the top of the page), and we see that in this portion, the contrast in sample structure is revealed. For metallic materials which undergo surface oxidation simply with exposure to the air, the ability to produce a fresh surface in the SEM chamber is a great advantage.

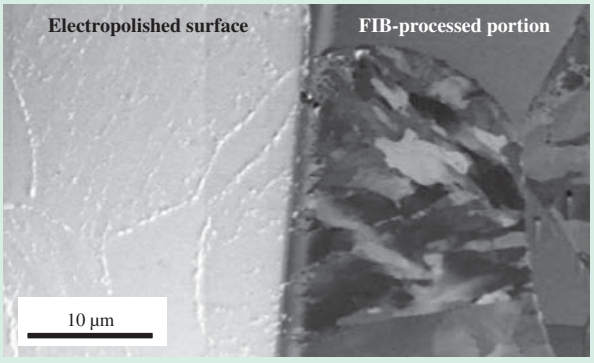

Fig. 3—Steel Material Surface-finished by Electropolishing. The figure shows an electropolished surface (left), and the same surface cut by FIB (right).

SEM Image "Depth" Resolution

When considering the spatial resolution of three-dimensional reconstructed images obtained by FIB-SEM serial sectioning, it is necessary to take account of the slice thickness (z direction) as well as the probe diameter. The z-direction resolution is dependent on the performance of the FIB, being determined by the pitch of FIB slices. However, because the electron beam penetrates a long way into the specimen when using a high SEM accelerating voltage, the image also contains information from the depth direction, which defeats the purpose of having a narrow slice pitch. Accordingly, keeping the accelerating voltage as low as possible to minimize how far the electron beam spreads into the specimen is important for improving the spatial resolution in practice. The instrument is able to produce three-dimensional reconstructed images with an effective spatial resolution of 2 nm by performing SEM observations with a low accelerating voltage and using an FIB capable of precise milling.

Example of Three-dimensional Reconstructed Image Observation

As discussed above, the cut surface in FIB eliminates topographic contrast and enhances the internal microstructure of the specimen. To date, there are many examples of observation on this basis.

Fig. 4 is an example in a titanium molybdenum (Ti-Mo) alloy showing determination of the shape, distribution, volumetric ratio, and other aspects of precipitate, also known as "omega phase[(2)]." Omega phase greatly affects the mechanical characteristics of a β-titanium alloy but precipitates very finely and at high density, complicating quantitative evaluation. The SEM image shown in Fig. 4 (a) is an observation by an in-lens type secondary electron detector made at an accelerating voltage of 2 kV. Because the molybdenum content of omega phase is low with respect to the matrix, at approximately 5%, its density difference is observable as dark contrast. Fig. 4 (b) is a three-dimensional reconstruction of 260 SEM images produced with a slice thickness set at 2 nm. The result is that the volumetric ratio, size, shape, and other aspects of omega phase particles can be evaluated quantitatively. Consequently, because the FIB cut surface is perpendicular to the SEM optical axis, baseline contrast is uniform, and even slight differences in composition can be enhanced to allow observation. Fig. 5 (a) is an example of observation of the distribution of precipitate particles observed near the interphase interface of δ-ferrite and tempered

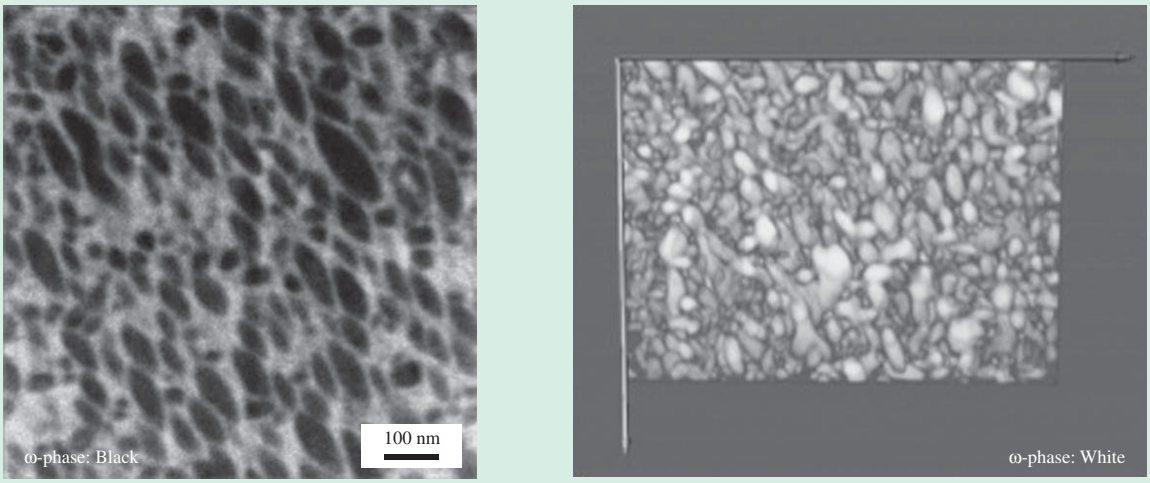

Fig. 4—Observation of ω-phase in Ti-Mo Alloy.
(a) shows a two-dimensional image used in serial sectioning, and (b) shows the three-dimensional reconstructed image.

martensite in iron-chromium (Fe-Cr) based heat-resistant steel[3]. Because the contrast in the image is high, once a type of precipitate is identified by EDS, many types of precipitates can be distinguished by contrast alone. Fig. 5 (b) is an observation made to determine how a vanadium-based carbonitride (black) and a gray chrome-based carbide (gray) are distributed at their phase interface. Because precipitate distribution at the interface cannot be determined accurately either through projected image observation by TEM or through surface observation by SEM, high-contrast, three-dimensional image observation is an extremely effective means for such determination. Such observation is also progressing from material specimens to biological specimens. Fig. 6 is an example of observation during serial sectioning of

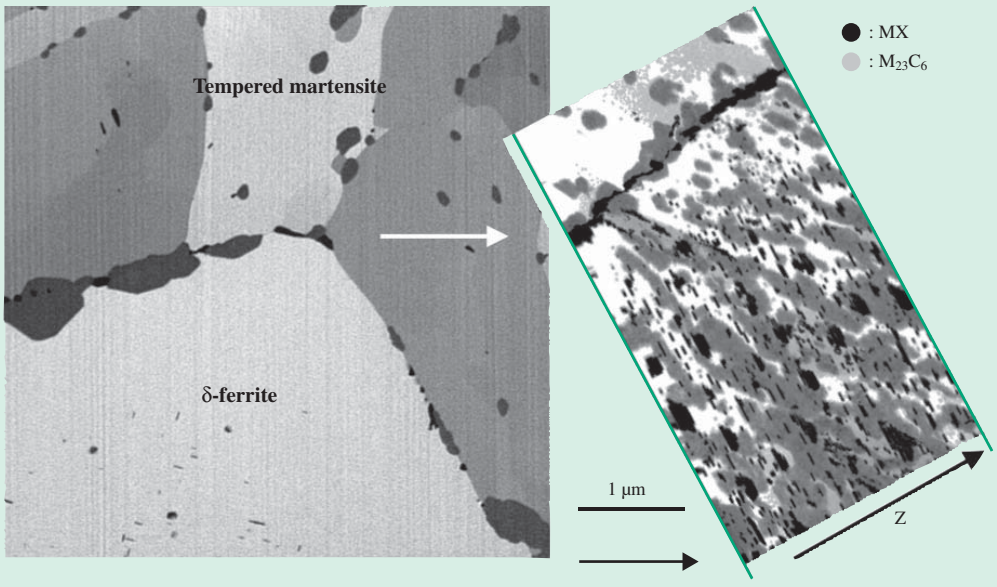

Fig. 5—Observation of Precipitate Distribution in Heat-resistant Steel.
(a) shows an SEM image during serial sectioning observation, and (b) shows the precipitate distribution at δ-ferrite - tempered martensite interface (oriented toward depth of printed sheet).

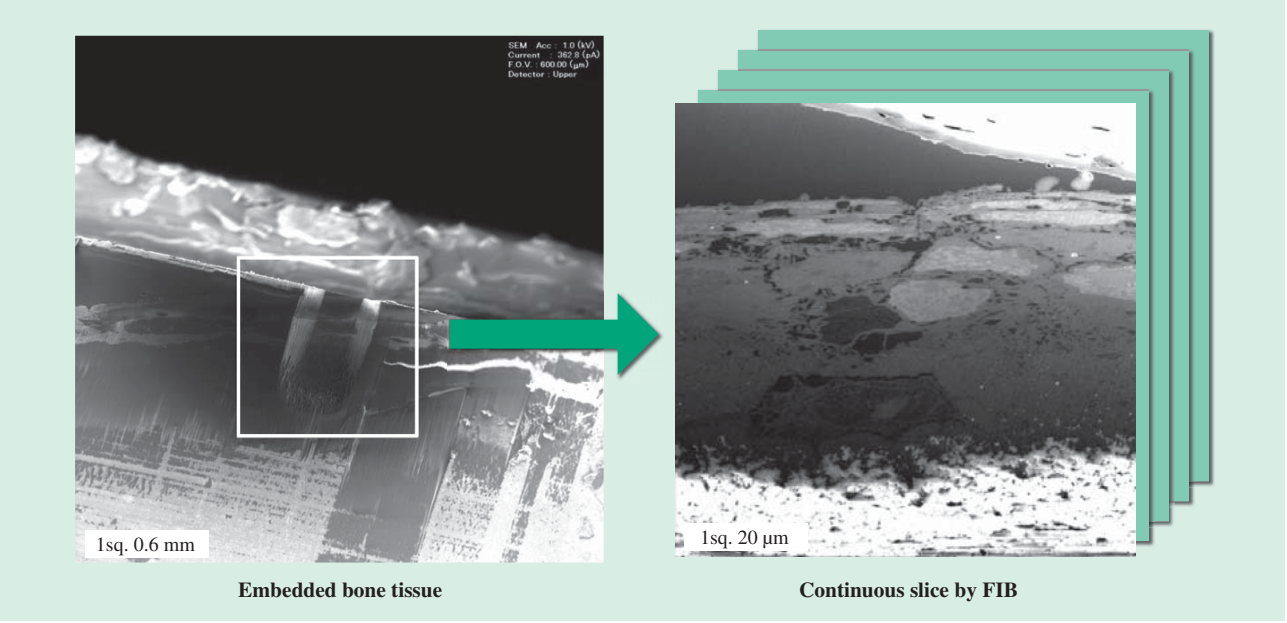

Fig. 6—Serial Sectioning Observation of Bone Tissue.
The location to be observed can be found using low magnification and a wide field of view, as in the image on the left. The edge in the middle of the image is the surface of a chick embryo skull, with the downward direction in the image corresponding to depth. The image on the right shows the field of view used to reconstruct the three-dimensional image.

bone tissue. Embedded chick embryo skull is observed from the surface layer to a deep region. In this instance, the site of desired observation is brought to the edge of the sample, which is sliced on a direct horizontal by FIB. Accelerating voltage of 1 kV allowed good imaging[4]. In another example, when measuring the shape or volumetric ratio of spaces in a specimen with many spaces, such as a battery electrode material, the spaces should be filled with a resin or the like for observation, but in many cases, this cannot be done. Various innovations have therefore been devised. For example, serial sectioning is performed without resin filling, and with the specimen in its original shape or state; multiple images are acquired with different observational parameters for each slice; and the shape or ratio of spaces is determined using innovative observational parameters or analytical techniques, such as binarization of spaces and specimen material in image processing[5].

EXPECTATIONS FOR FUTURE DEVELOPMENT

As described, this instrument, with its perpendicular FIB and SEM configuration, is ideal not only for observation of three-dimensional reconstructed images produced by serial sectioning; it is also effective for observing the internal microstructure of a specimen through observation of a surface cut by FIB. To date, many diverse specimens have been observed successfully, but observation with greater precision and sensitivity will require further innovation in many respects. The commonality of these needs in many cases is a frequent request from users for a task that is difficult today. Rather than ultra-high-resolution, requests take the form of greater general utility or greater multifunctionality, for example, "observation on a larger scale," "expansion of the types of applicable specimens," and "delivery of a greater variety of information." Without compromising the characteristics imparted by the perpendicular configuration, we anticipate future development seeking more advanced levels of such structural analysis to proceed as follows.
(1) Additional FIB methods for slicing. Specifically, techniques for cutting over a greater range, for example, techniques for cutting a milli-unit range at a nanoscale pitch. These developments represent great prospects for expanding observational area and shortening observation times.
(2) Efforts to address a variety of specimen requirements. Many samples are prone to charging in SEM, damage in FIB, or are otherwise unsuited to FIB-SEM. Other samples require cooling, heating, or other atmospheric control.
(3) Techniques for effective collaboration through simultaneous acquisition of various information.

Specifically, augmentation with diverse image detectors, and installation of microcalorimeter EDS or other such detectors for high-precision analysis unavailable to date.

(4) Acquisition of previously missed information. For example, when various information is acquired simultaneously, better analytical techniques allowing extraction of required information alone.

As users in need of structural analysis, we look forward to realization of these developments.

ACKNOWLEDGMENTS

Observational data for bone tissue in this manuscript were received from Prof. Hiroshi Kamioka and Dr. Rumiko Takamiya from Okayama University Graduate School of Medicine, Dentistry and Pharmaceutical Sciences. The analytical techniques using the instrument also derive from experiments and discourse among many users, whom we note and thank here.

The instrument was announced on the National Institute for Materials Science (NIMS) Microstructural Characterization Platform (http://www.nims.go.jp/nmcp/) "Nanotechnology Platform Japan" project by the Ministry of Education, Culture, Sports, Science and Technology, where it was described as "multi-scale analytical equipment for three-dimensional microstructures."

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Special Contributions

Development of High-performance Zeolite Catalysts for Effective Use of Carbon Resources

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Takashi Tatsumi, Dr. Eng.

OVERVIEW: If the resource, energy, and environmental problems facing the world are to be overcome, it is important that effective use be made of different types of resources. Given the problems of dwindling oil resources in particular and of reducing emissions of CO_2, establishing ways of making effective use of both conventional and unconventional carbon resources is a particularly crucial challenge. With "Environmentally conscious manufacturing – catalysts are the key" as a catchphrase, the authors have focused their research on zeolites, a class of microporous crystalline aluminosilicates with molecular-scale voids in their crystal structures. This article describes their recent work on the development of zeolite catalysts for the effective use of carbon resources.

INTRODUCTION

ZEOLITES[1), 2)] are microporous crystalline minerals that are subject to a high level of nano-scale control and that contain voids of uniform size at the molecular scale (0.3 to 1 nm) (see Fig. 1 and Fig. 2). These structural characteristics give zeolites three notable properties, namely their ability to be used as molecular sieves, ion exchangers, and solid acid catalysts. They have crystal particle diameters in the range of several micrometers and their external surface area is only a few percent of their total surface area. This means that most of their activity is accounted for by their micropores, and when reactants and products have sizes similar to that of the zeolite micropores, the rate and selectivity of the reaction are influenced by the geometrical relationship between the respective shapes of the micropores and the molecules. This

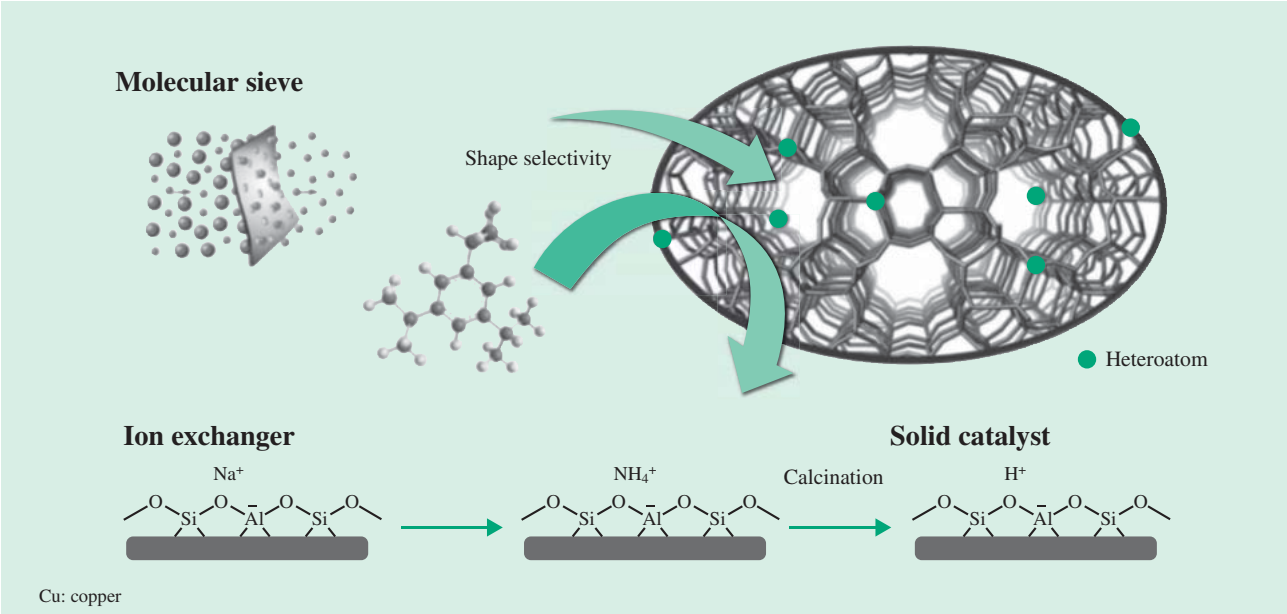

Fig. 1—Properties of Zeolites.
Zeolites are microporous crystalline minerals that are subject to a high level of nano-scale control and can be used as molecular sieves, ion exchangers, and solid catalysts.

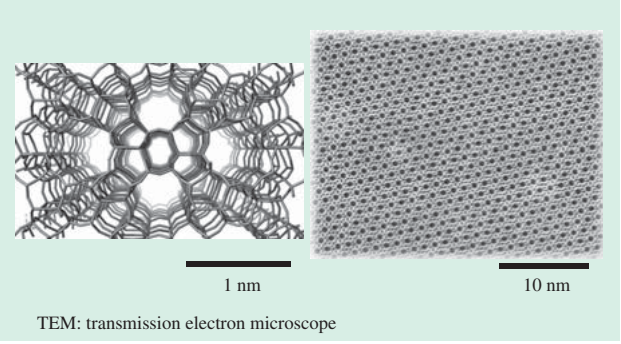

Fig. 2—Structural Model of MFI-type Zeolite (left) and TEM Image (right).
Each stick in the structural model represents a ≡Si-O-Si≡ sequence. The TEM image shows how the zeolite is made up of a regular array of identical micropores.

is called shape selectivity and allows zeolites to act as a molecular sieve, one of their main properties. Most zeolites have a silica framework and are aluminosilicates in which some of the silicon (Si) atoms are replaced with aluminum (Al) atoms. As some other cations are required to maintain the charge balance between Si^{4+} and Al^{3+}, this enables zeolites to act as ion exchangers and solid acid catalysts. Zeolite catalysts are currently used in environmental treatment systems as well as in the production of basic chemical feedstock from oil. Potential is also seen for their use in catalyzing reactions for chemical synthesis by the conversion of biomass.

This article focuses on the use of zeolites as solid acid catalysts and describes the development of a zeolite catalyst for making effective use of carbon resources.

PROCESS FOR CATALYTIC CRACKING OF NAPHTHA

Lower olefins such as ethylene, propylene, and butenes are important petrochemical precursors that are mainly produced by the thermal cracking of naphtha. However, there is also interest in catalytic cracking using zeolite as the catalyst because it allows the reaction to proceed at a lower temperature and can achieve a propylene/ethylene ratio of 0.6 or higher[3), (4)]. Unfortunately, catalytic cracking suffers from problems such as acid sites becoming coated due to the production of coke and a loss of catalytic activity due to blocking of the micropores. It has been reported in the past that catalyst life can be improved in various hydrocarbon conversion reactions by increasing the number of entry and exit points to the micropores by enlarging the external surface area, or by shortening the diffusion length by making the zeolite crystals smaller and creating mesopores inside the crystal[(5), (6)]. The authors, too, have identified ways of extending the life in catalytic cracking of hexane through the use of nano-sized catalysts by using alkali treatment to form mesopores and control acidity[(7), (8)]. Recently, they have developed a method for controlling the distribution of Al inside Zeolite Socony Mobil–5 (ZSM-5) micropores and have been working specifically on the influence that the positioning of Al inside the micropores has on acid catalyst activity[(9)].

How to minimize catalyst deactivation is an important factor in the catalytic cracking of naphtha. Reasons for this deactivation include structural breakdown, leaching of the Al atoms in the zeolite framework that serve as the site of activity, coating of the site of activity due to the formation of coke, and blocking of the micropores. To solve these problems, it is important to obtain information about the structure and distribution of active sites and about where coke is formed. This means it is helpful if detailed observations can be made of the cross-section of zeolite particles. The authors have analyzed the elements present inside particles of zeolite using an ion milling machine to image the cross-section of zeolite catalysts and using energy-dispersive X-ray spectroscopy (EDX) to determine composition. The following describes an example.

Assessing Coke Distribution Using Cross-sectional Imaging of Zeolite Catalysts

A hexane catalytic cracking reaction over ZSM-5, a zeolite catalyst of framework type MFI, was performed at 650°C. The quantities of coke that had built up on the catalyst after reaction times of 3, 6, and 12 hours were determined by thermogravimetric (TG) analysis to be 5.3 wt%, 6.8 wt%, and 8.8 wt% respectively. Differential thermal analysis (DTA) was also used to determine that the peak exothermic temperatures gradually increased from 600°C to 630°C and 640°C. From this it was concluded that an increasing amount of coke builds up on the ZSM-5 catalyst over the course of the reaction, and that the coke is transformed into other less combustible forms of carbon (with higher molecular mass). This left the question of where the coke was forming on the ZSM-5 catalyst. Was it happening in the micropores of the zeolite or on the outer surfaces of the particles? To investigate this, an ion milling machine was used to view a cross-section of the zeolite catalyst and EDX used to analyze its composition. The main

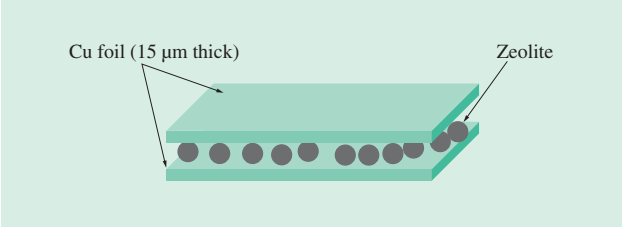

Fig. 3—Sample Preparation for Carbon Mapping.
The sample is held together by sandwiching powder between sheets of Cu foil and a cross-section prepared by ion milling.

objective was to perform mapping of coke (carbon). Because the pastes normally used to hold powder in place contain carbon, they are unsuitable for mapping coke. As shown in Fig. 3, the sample was instead prepared by sandwiching it between sheets of copper (Cu) foil for ion milling and EDX analysis.

Fig. 4 shows the carbon maps for an ZSM-5 particle cross-section after reaction times of 3, 6, and 12 hours. These show that, as the reaction progresses, more coke is formed along the outside of the crystal than in its interior. This indicates that the coke is mainly forming on the outer surface or near the micropore entrances, not inside the micropores. Particularly large amounts of carbon were detected from the surface to approximately 400 nm into the interior, with the concentration of carbon near the surface increasing the longer the reaction progressed. However, it was also found that large amounts of coke formed over time in the interior. Currently, the authors are using this to try different catalysts and modify the reaction to build up more knowledge about coke distributions that can be incorporated into catalyst design and used to develop catalysts with longer lives.

DEVELOPMENT OF ZEOLITE CATALYST FOR PRODUCTION OF LOWER OLEFINS FROM NON-OIL RESOURCES

As noted above, the establishment of an alternative to the thermal cracking of naphtha that can produce lower olefins without imposing a large load on the environment plays an important role in terms of making effective use of carbon resources. And, given the problem of future oil scarcity, there is a need to create a process for producing propylene from non-oil resources. This has included interest in methanol-to-olefin (MTO) reactions that produce substances such as propylene and ethylene using methanol as a feedstock. As the methanol feedstock is produced by reacting hydrogen (H_2) with carbon monoxide (CO) or carbon dioxide (CO_2) derived from natural gas or coal, this provides a way to produce lower olefins from resources other than oil.

Zeolite catalysts that demonstrate good performance in MTO reactions include ZSM-5, the MFI-type zeolite with medium-sized micropores; SSZ-13 with small micropores; and SAPO-34, a CHA zeolite[10]. However, issues remain with things like lower olefin selectivity and catalyst life and this is currently an active field of research. The authors have succeeded in developing a new CON-type zeolite catalyst that is different from typical catalysts for the MTO reaction. The CON-type zeolites have a unique structure that combines both large and medium-sized micropores. While this gives the catalyst the potential to be used in a wide variety of applications, it has not been widely studied in the past because it is difficult to synthesize. The authors have made improvements to the synthesis

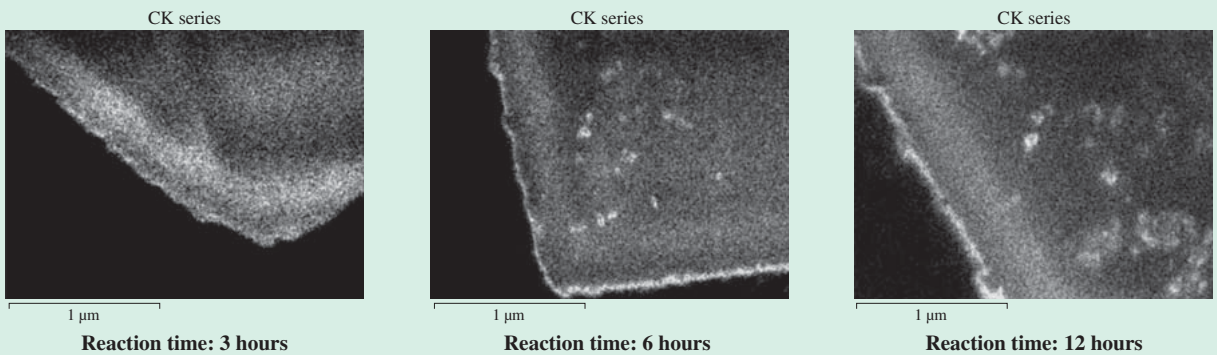

Fig. 4—Distribution of Coke Adhering to ZSM-5 Zeolite Catalyst after Catalytic Cracking of Hexane.
These carbon maps show the ZSM-5 particle cross-sections after reaction times of 3, 6, and 12 hours. They show how the amount of coke adhering to the outer surface of the particles becomes larger over time.

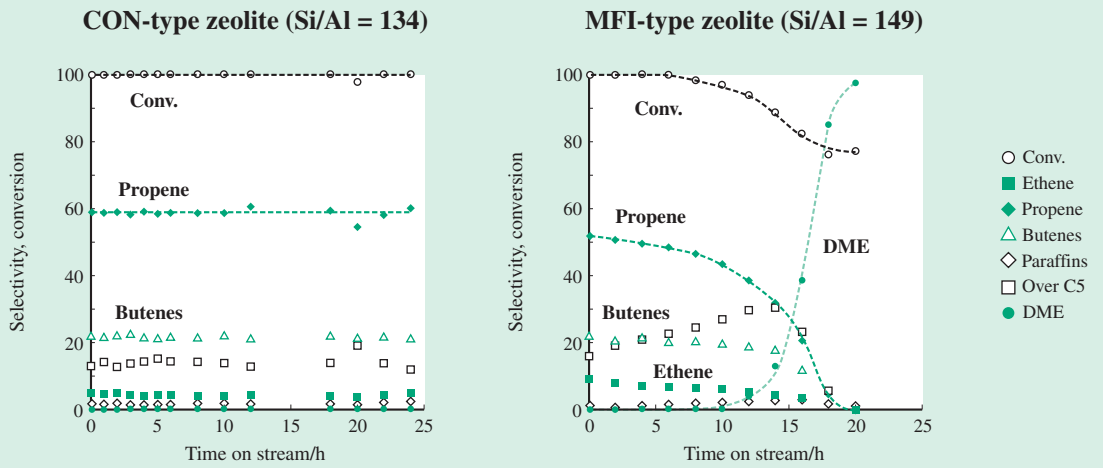

Fig. 5—Results of MTO Reaction Using the CON- and MFI-types Zeolites.
The CON-type zeolite maintains a methanol conversion rate of close to 100% even after 25 hours. It also maintains a propylene selectivity of approximately 60%.

process and developed a technique for introducing Al into the CON zeolite framework that will enable it to be used as an acid catalyst[11].

Compared to previous MFI-types, the Al-containing CON-type zeolite is characterized by low ethylene selectivity, high propylene and butenes selectivity, and longer catalyst life (see Fig. 5). Propylene and butenes selectivities are respectively a little under 60% and a little over 20%, high values in comparison to the less than 5% selectivity for ethylene.

The authors are currently participating in an artificial photosynthesis project of the New Energy and Industrial Technology Development Organization (NEDO) and the Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem)[12]. This project aims to use the MTO reaction to produce lower olefins from methanol that has been made from solar hydrogen produced from water using a photocatalyst and the energy of the sun, and CO derived from CO_2 emitted by industrial processes and other sources. In other words, its objective is to make plastics from water by using artificial photosynthesis to enable the manufacture of chemicals without the use of fossil fuels.

CONCLUSIONS

This article has focused on zeolites in their role as solid acid catalysts, describing the catalytic cracking of hexane and the synthesis of propylene from methanol. These catalytic processes help make the most of carbon resources and are helping overcome the resource, energy, environmental, and other problems facing humanity. If ways could be found to achieve full control over the type, strength, and quantity of acid on zeolite catalysts as well as their micropore structure and particle morphology, the authors believe this would not only lead to improvements in catalyst performance but also expand the range of applications. While there are many problems with zeolite catalysts that remain to be solved, it is hoped that solutions will be found so that they can enter industrial use in a variety of fields.

ACKNOWLEDGMENTS

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Special Contributions

Advanced Biomedical Transmission Electron Microscopy

Akira Sawaguchi, M.D., Ph.D.

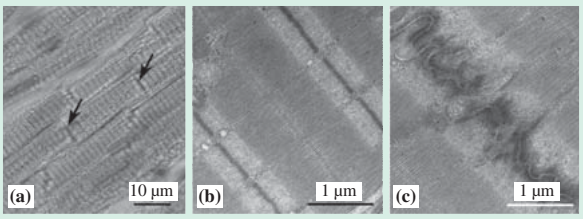
OVERVIEW: Transmission electron microscopy provides resolutions that greatly exceed what is possible on optical microscopes, and the post-genomic era of recent years has seen the emergence of new developments in the application of this technology to biomedical research. In addition to microstructural changes to cells in knockout organisms (in which a particular gene has been disabled), huge demand is emerging for verifying the microscopic structure of cells and tissue grown from iPS cells, a type of stem cell that has unlimited potential to differentiate into every other kind of cell. This article looks ahead to the next generation of microscopes to present the latest information about how, in response to these new developments, the most recent transmission electron microscopes have made dramatic advances in their roles as precision instruments that are simple and easy to use, incorporating functions for auto-focus, fully digital photography using CCD cameras, and image transmission via video conferencing system.

INTRODUCTION

HUMAN beings are very acquisitive animals who want to magnify objects that are too small to see with the naked eye and to break open those that are encased in something so as to expose them to view. It is this acquisitiveness that is behind the use of transmission electron microscopes in biomedical research to uncover the fine structures encased in cell membranes at a microscopic level. This article brings the perception of transmission electron microscopy up to date, using the HT7700 transmission electron microscope made by Hitachi High-Technologies Corporation as a basis for providing an introduction to this technology, which has evolved to meet the needs of biomedical research. The article delves into the origins of transmission electron microscopy, including its use in topical research into induced pluripotent stem (iPS) cells, and proposes a new generation of the technology that will satisfy the demands placed upon it.

ADVANTAGES OF TRANSMISSION ELECTRON MICROSCOPY WITH HIGH SPATIAL RESOLUTION

Optical microscopes can provide bright images of fluorescent markers. It is the high spatial resolution of electron microscopes, however, that is their most notable feature compared to optical microscopes, and this feature continues to provide unshakeable scientific evidence despite their being limited to monotone images. As a simple example, whereas it is possible to just make out the distinctive stripes and linear features of intercalated disks [shown by the arrows in Fig. 1 (a)] in myocardial fiber in the optical



H&E: hematoxylin and eosin

Fig. 1—Comparison Images Demonstrating the High Resolution of Electron Microscopes (Rat Heart Muscle).
Image (a) was taken by an optical microscope using H&E staining and a ×100 oil-immersed objective lens. The distinctive striped pattern of heart muscle and the linear shape of the intercalated disks are visible (shown by the arrows). Images (b) and (c) were taken by a transmission electron microscope using uranium and lead staining. Image (b) shows the regular arrangement of actin and myosin in the myocardial fiber, and image (c) clearly shows the microscopic structure of the intercalated disks, which perform an important function in the beating of the heart, with localized joints in the gap.

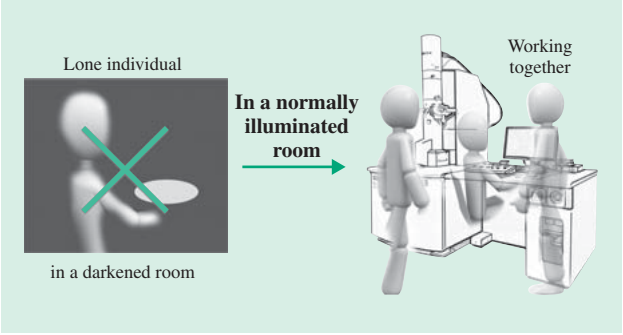


Fig. 2—Viewing Electron Microscope Images on a Monitor. Use of an electron microscope has changed from being something done by a lone individual in a darkened room to a collective activity in a normally illuminated room.

microscope image of a rat heart muscle, transmission electron microscope images enable more detailed examination, including showing the fibrous structure of the actin and myosin that make up the stripes [see Fig. 1 (b)] and the complex shape of an intercalated disk [see Fig. 1 (c)].

ADVANCED TRANSMISSION ELECTRON MICROSCOPIC OBSERVATION AND PHOTOGRAPHY

Simple Operation in Normally Illuminated Room Together with Colleagues

Using a fluorescent screen to display cell morphology imaged by an old-style transmission electron microscope using an electron beam requires the room to be dark. Transmission electron microscopes were typically installed in back rooms away from sunlight and tended to be used by a single individual shut away in a darkroom as the fluorescent screen on the other side of the observation window into the scope did not allow for group viewing. This image is now out of date. On the latest transmission electron microscopes, the image on the fluorescent screen is captured by a screen camera and displayed on a monitor, meaning it is no longer necessary to peer into a fluorescent screen in a darkroom. Instead, images can be viewed together with colleagues in a normally illuminated room (see Fig. 2). Nowadays, transmission electron microscopes are installed in rooms with glass windows fronting onto corridors so that people can see the microscope in action as they pass by.

Auto-focus that Works Like a Digital Camera

It is not just beginners who struggle with focusing and find themselves having to re-take photographs after discovering that the membrane structure in the developed image is indistinct. The latest transmission electron microscopes, by contrast, have made this a thing of the past, coming equipped with an auto-focus function that takes only a few seconds to focus the image automatically. In other words, electron microscope imaging can now be performed in much the same way as using a digital camera (see Fig. 3). The ability to view images and assess their quality immediately has also provided a step up in operational efficiency.

Digital Images that do not Need to be Developed and Smart Image Data Management

The elimination of film associated with the switch to digital imaging means it is no longer necessary for people to strain their eyes developing images under the safety light in a darkroom. Furthermore, image recording systems include a helpful captioning function that can be used to record experimental

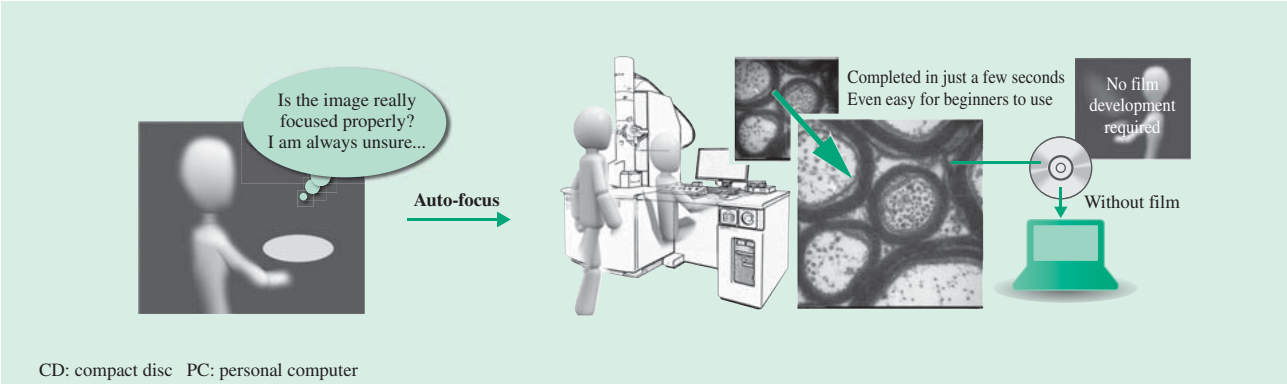


Fig. 3—Electron Microscope Image Acquisition Using Auto-focus and without Film. Images are stored on CD and can be viewed or saved on a PC.

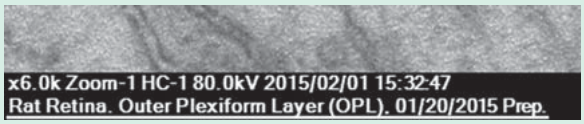
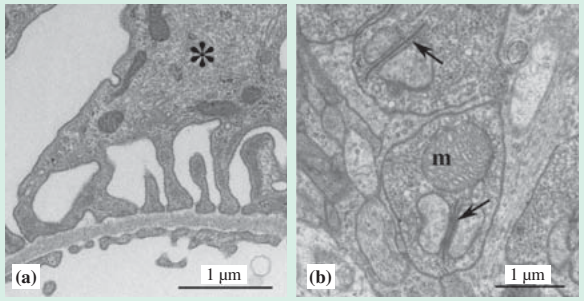


Fig. 4—Captioning Function.
The captioning function shown here is useful for recording and cataloging electron microscope images. Comments can be inserted as required in a field at the bottom of the image (white underlined text).



HC: high contrast CCD: charge-coupled device

Fig. 5—HC Mode and High-performance CCD Camera.
The high-performance CCD camera can capture adequate images using Reynolds lead staining rather than uranium staining. Image (a) shows a podocyte (indicated by the asterisk) in the glomerulus of a rat kidney. Image (b) shows the outer plexiform layer of a rat retina. A mitochondrion (indicated by the "m") and synaptic ribbon (indicated by the arrow) are clearly visible.

data, comments, and other information as required (see Fig. 4). Database management functions are also available to simplify the cataloging of large numbers of recorded images as well as search and retrieval.

High-performance CCD Camera that Eliminates the Inconvenience of Using Uranium Staining

The high-contrast (HC) mode of the compound objective lens in the HT7700 together with the high-quality imaging achieved using the high-performance charge-coupled device (CCD) camera provided as a standard feature mean it can achieve adequate contrast using lead staining only, thereby eliminating the need for the uranium staining that was once common practice (see Fig. 5). As uranium is a difficult material to obtain, being subject to strict conditions, including those relating to the storage of waste fluid after use, this improvement represents a major step toward encouraging applications for transmission electron microscopy.

Significant Boost in Efficiency Provided by Stage Memory Function and Three-Specimen Holder

The restricted field of view available with transmission electron microscopy means that it is not uncommon to lose track of where on the specimen cross section the microscope is looking and so to lose the ideal point of observation after it has been identified, like being lost in the woods because one can only see the trees. However, this too is now a thing of the past. The latest transmission electron microscopes such as the HT7700 are equipped with a stage memory function that records the movements of the specimen stage and eliminates the problem of losing the observation location (see Fig. 6). The microtrace function, meanwhile, which displays the sequence of specimen stage movements, can be used to see which parts of the specimen have or have not been viewed.

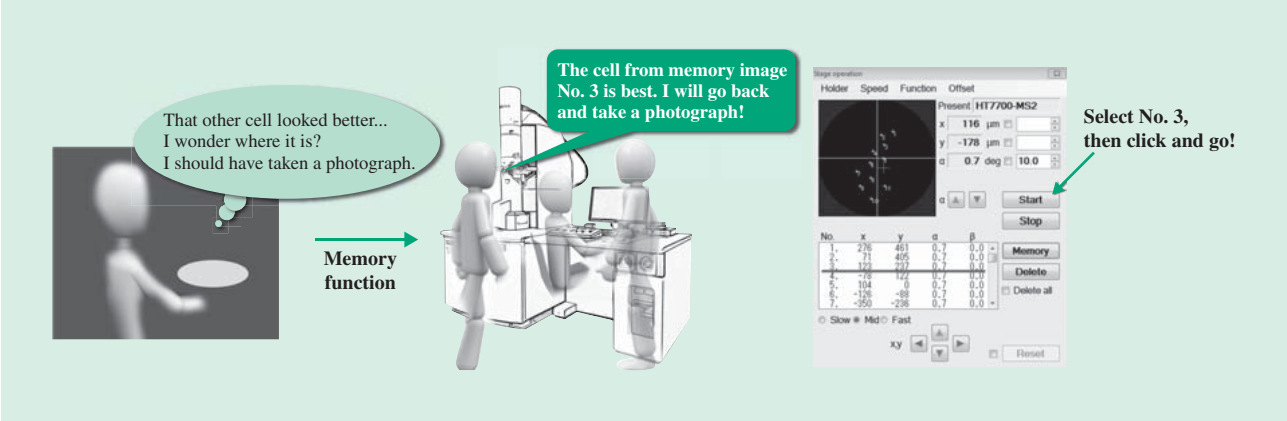


Fig. 6—Stage Memory Function.
The stage memory function avoids missing out on the best images.

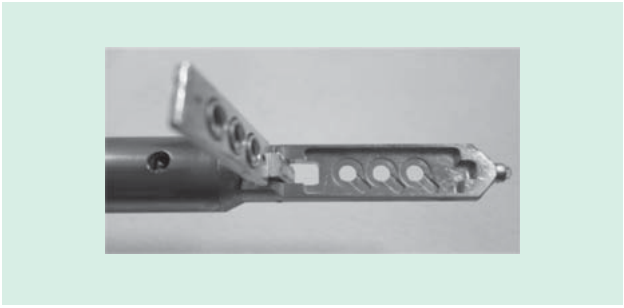


Fig. 7—Three Specimen Holder.
Three grids can be inserted at a time using the convenient three specimen holder. This significantly improves efficiency by reducing the amount of effort spent on swapping grids.

Transmission electron microscopy requires the insertion and removal of specimens from the microscope barrel, which is maintained in a state of vacuum to obtain the electron beam. Accordingly, operational efficiency can be significantly improved by combining the stage memory function with the three specimen holder shown in Fig. 7 (available as an option), which can be used to insert three specimen-containing grids at a time.

Powerful Support for Joint Research Provided by Electron Microscope Image Transmission and Videoconferencing System

An electron microscope image transmission system that uses the latest information technology can send electron microscope images acquired by the screen camera or high-performance CCD camera to designated recipients on the Internet. Used in conjunction with a videoconferencing system, this makes it possible to share electron microscope images in realtime while holding a discussion with a remotely located joint research team. The electron microscope image transmission system keeps tight control over information security. Transmission electron microscopy is set to move from a solitary person working on their own in a darkened room to an era in which people work with colleagues in a normally illuminated room and are able to share images with others located remotely (see Fig. 8).

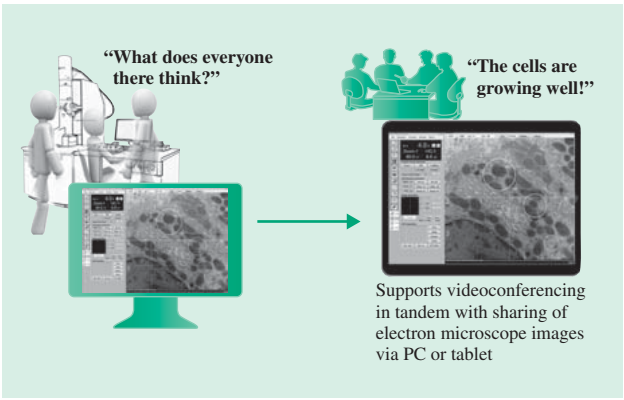


Fig. 8—Use with Videoconferencing System.
It is now possible to share images while holding discussions with a joint research team at a remote location.

SIMPLE, QUICK, AND RELIABLE —DRAMATICALLY IMPROVED SPECIMEN PREPARATION FOR TRANSMISSION ELECTRON MICROSCOPES—

A negative perception associated with transmission electron microscopy is that it requires complex and time-consuming specimen preparation, and while there are many cases in which it can be avoided, simple, quick, and reliable specimen preparation techniques have now been produced into which a wide variety of practices have been incorporated[(1)-(3)]. To enable specimens acquired in the early morning to be observed under a transmission electron microscope on the evening of the same day (see Fig. 9), workflows have started to be adopted in practice that involve the routine use of a transmission electron microscope for screening samples and then subjecting the selected samples to molecular biological analysis, an approach that was rejected in the past as impractical.

How many users have experience of repeatedly preparing and observing ultra-thin sections until a suitable cell is identified? This is another outdated practice. The way things are done now is to use an

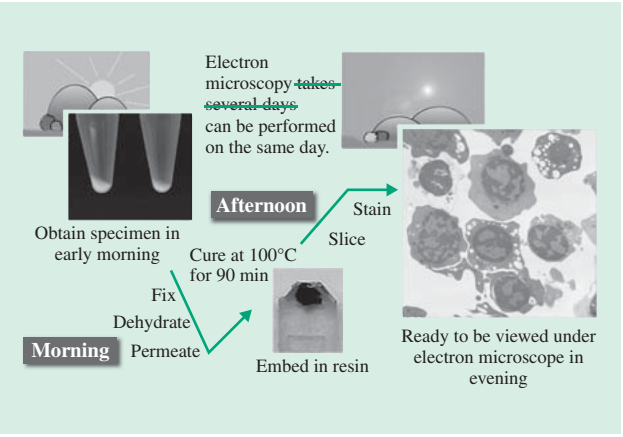


Fig. 9—Improved Specimen Preparation Technique.
It is now possible to collect a specimen in the early morning and view it under a transmission electron microscope that same evening.

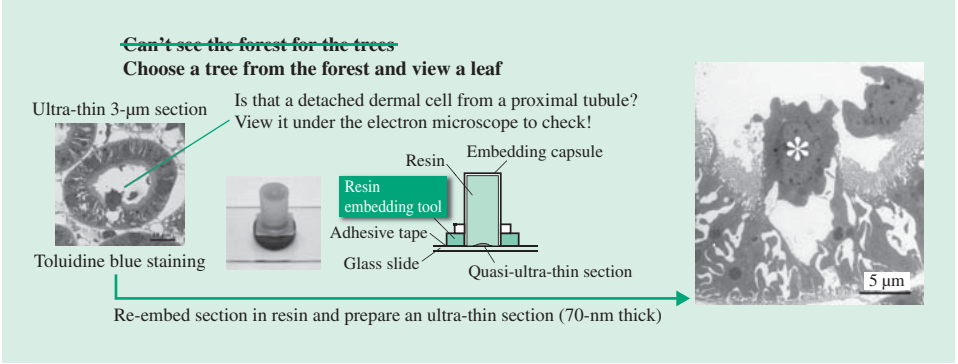


Fig. 10—Using an Optical Microscope to Select Ultra-thin Section for Viewing Under Transmission Electron Microscope.
It is possible to use an optical microscope to pinpoint a target cell and then study it under a transmission electron microscope.

optical microscope to screen quasi-ultra-thin sections, and then to re-embed them in resin and slice an ultra-thin section for viewing under a transmission electron microscope[2), (3)]. This is because it is easy to use a transmission electron microscope to image a cell once it has been identified as the target using the optical microscope (see Fig. 10).

PROPOSAL FOR NEXT GENERATION OF BIOMEDICAL TRANSMISSION ELECTRON MICROSCOPY—CONCLUSIONS—

Transmission electron microscopy, which provides resolutions that greatly exceed what is possible on optical microscopes, has made an incalculable contribution to biomedical research. During the burgeoning of research techniques for molecular biology in the 1990s, research based primarily on the electron microscope was derided as being outdated and old-fashioned, like scavenging for rice in a paddy field that has already been harvested. The author, who had a secret fascination with a certain medical cartoon character, will never forget having been told this upon swapping a scalpel for an electron microscope and choosing the path of anatomical research. The words were spoken by an older colleague who was a self-described molecular biologist.

A quarter century has passed since then. New developments have emerged as the world enters a post-genome-sequencing era. Transgenic organisms have been created as well as knockout organisms such as mice in which a particular gene has been disabled, and these have required comparative studies to look at what changes are present in the fine structure of cells and tissue. Furthermore, the development of iPS cells has given rise to huge demand for verifying the microscopic structure of cells and tissue grown from iPS cells, which can differentiate to form every other kind of cell.

One such example of this verification is the undertaking of basic research into the production of platelets from IPS cells designated in the Ministry of Education, Culture, Sports, Science and Technology's iPS Cell Research Roadmap, which is approaching the stage of large-scale production for clinical applications. In a paper on the establishment of this core technology[4], transmission electron microscopy made a major contribution, with the need for it made obvious by Fig. 11, in which the platelets are very small compared to the red blood cells and neutrophils and would appear as mere dots under an optical microscope. In contrast, the open canalicular system and secretory granules inside platelets are clearly visible using transmission electron microscopy [see Fig. 11 (b) and (c)]. The diameter of platelets is only in the range of 1 to 2 µm and transmission electron microscopy is essential for the detailed observation of their internal structure.

Currently, studies into clinical applications in areas such as regenerative medicine and drug development, based on using iPS cells to produce cells, tissue, and

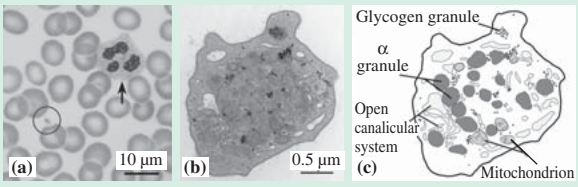


Fig. 11—Human Platelets.
Image (a) is a peripheral blood smear and was taken with an optical microscope using Giemsa staining. The small object indicated by the circle is a platelet, the arrow indicates a neutrophil, and the nearby circular cells are red blood cells. Image (b) is from a transmission electron microscope using lead staining and image (c) is a schematic diagram of the internal structure.

organs of many different types, are proceeding in parallel with the establishment of an all-Japan research regime. What was once equivalent to scavenging for rice in a paddy field that has already been harvested has now become a new era where there is a prospect of harvest (electron microscopy), with the ears of grain (cells induced to differentiate from iPS cells) laden with a new variety of rice (iPS cells) in a newly reclaimed paddy. It is a field where, rather than using scanning electron microscopes for imaging the surface of cells, it will be the use of transmission electron microscopes for imaging their interior that will play the major role. From specimen preparation to observation and image acquisition, this transmission electron microscopy is evolving into a precise analytical technique that is simple and convenient. The author would like to conclude this article by looking forward to electron microscopes raising the standard of the latest biomedical research and opening up new fields of research.

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Special Contributions

Development of SEM for Realtime 3D Imaging and Its Applications in Biology

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Futoshi Iwata, Ph.D.
Wataru Kotake
Sukehiro Ito

OVERVIEW: We have developed a device for displaying TV-rate 3D images on a monitor by tilting the electron beam of an SEM to the left and right for each scan line to acquire dual (stereoscopic) images simultaneously. It has also improved the resolution of stereoscopic imaging by developing optics that minimize the off-axial aberrations that are associated with this electron beam tilting. Among the benefits of this realtime stereo SEM is that 3D imaging makes it possible to manipulate the sample under observation. Its effectiveness for this purpose was demonstrated by installing a prototype micro-manipulator in an SEM sample chamber and using it in a realtime stereo SEM to perform microanatomical dissections on biological samples.

INTRODUCTION

THE ability of scanning electron microscopes (SEMs) to image the three-dimensional (3D) surface structure of samples has numerous applications in the life sciences as well as in materials science. They are particularly valuable in medical biology where they are used to study the fine 3D structures of cells or tissues, which are difficult to analyze under a transmission electron microscope[1].

Unfortunately, conventional SEMs are only able to view or capture monocular images in the manner of a camera that takes a single photograph. Accordingly, attempts have been made since SEMs first entered practical use to achieve binocular vision by taking two separate images of the same field of view from different angles (stereoscopic images) and then viewing them either with a parallel or cross-eyed method to achieve 3D imaging. Unfortunately, the complexities of obtaining stereoscopic images and the difficulties of stereoscopic display have meant that applications for 3D imaging have been limited up to now. Furthermore, conventional SEMs are not capable of 3D imaging in realtime. Although some attempts at realtime 3D viewing by SEM have been made, they have not been considered to be of much practical use due to reasons of resolution or ease-of-operation.

Recently, however, advances in SEM technology together with progress in computing and display techniques have ushered in a new era in 3D imaging for SEMs. Accordingly, we decided to embark on development work aimed at achieving a genuinely practical implementation of a realtime stereo SEM, and along with pursuing this development, have commercialized some of the results of this work. This article explains the principles of 3D imaging on an SEM, presents an overview of the newly developed realtime stereo SEM, and introduces a demonstration utilizing the capabilities of an SEM for in-place sample manipulation.

STEREOSCOPIC 3D IMAGING BY SEM

As noted above, 3D imaging on an SEM requires two images, corresponding to the parallax of the human eyes. While there are some different ways in which these stereoscopic images can be obtained, the most common are: (1) tilting the sample to acquire images from different angles (stage tilting), and (2) changing the direction of the incident electron beam to acquire images from different angles (electron beam tilting)[2].

Stage Tilting

This technique involves tilting the sample stage to obtain images from two different angles corresponding to the angle of parallax [see Fig. 1 (a)]. Because any SEM capable of tilting the sample can obtain stereoscopic images, this technique has been used for a long time and can obtain high-resolution images[3]. However, obtaining images with the same field of view after tilting the sample is actually quite complicated and time-consuming, and the nature of this technique means it cannot be used for 3D imaging of the sample shape in realtime.

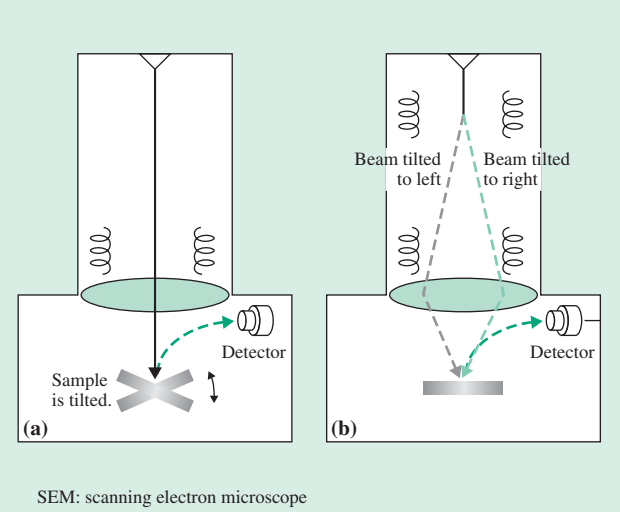


Fig. 1—Stereoscopic Imaging by SEM.
The figure shows how imaging is performed (a), by tilting the stage, and (b), by tilting the electron beam.

Electron Beam Tilting

This technique involves tilting the electron beam to obtain the stereoscopic images [see Fig. 1 (b)]. The technique first appeared in the 1970s in the form of an SEM capable of producing 3D images with a scan rate comparable to television (TV) images[4]. Unfortunately, a number of problems needed to be resolved before the technique could enter practical use, including the loss of resolution due to the off-axial aberrations induced by electron beam tilting and the problem of how to display the images in realtime.

DEVELOPMENT OF REALTIME STEREO SEM

Having chosen to use the electron beam tilting technique described above when it set out to develop a practical realtime stereo SEM capable of 3D imaging in realtime, we needed to find a way to obtain stereoscopic images with high resolution while minimizing the aberrations associated with electron beam tilting. It was also considered desirable that the images obtained be viewable with a TV scan rate. A way to display the 3D images was also required. Accordingly, we started by studying ways to obtain high-resolution stereoscopic images at high speed using electron beam tilting.

Development of Electron Beam Tilting Technique Using Focusing Action of Lens

To achieve high-speed acquisition of stereoscopic images, it is desirable that the images from the two different angles be obtained simultaneously by performing electron beam tilting for each line or frame. To achieve this, the electron beam is tilted at an angle of $t0$ by the tilt angle control coil and then focused by the objective lens so that it reaches the sample at an angle of $t1$, as shown in Fig. 2. Because the stereoscopic images can be obtained by this technique at a rate determined by the scanning speed, 3D imaging can be performed with a TV scan rate. Furthermore, because the electron beam can be tilted in any direction or at any angle, the image can be rotated for flexible 3D viewing without any need to rotate the sample mechanically. The practical implementation of an SEM that uses this technique makes possible realtime 3D imaging of biological tissue with complex structure, and enables the two stereoscopic images to be obtained simultaneously in a single operation (see Fig. 3).

In conventional SEM imaging, the electron beam is controlled so that it passes through the center (axis) of the objective lens. However, because electron beam tilting relies on the focusing action of the objective

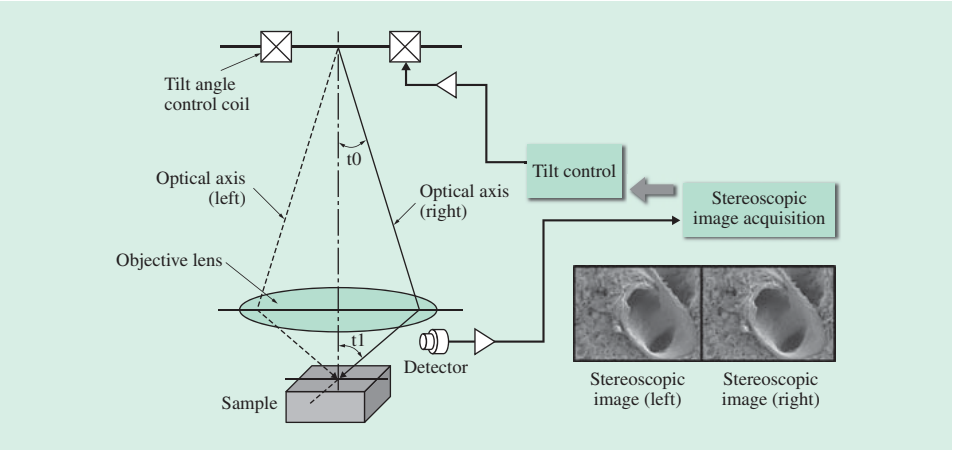
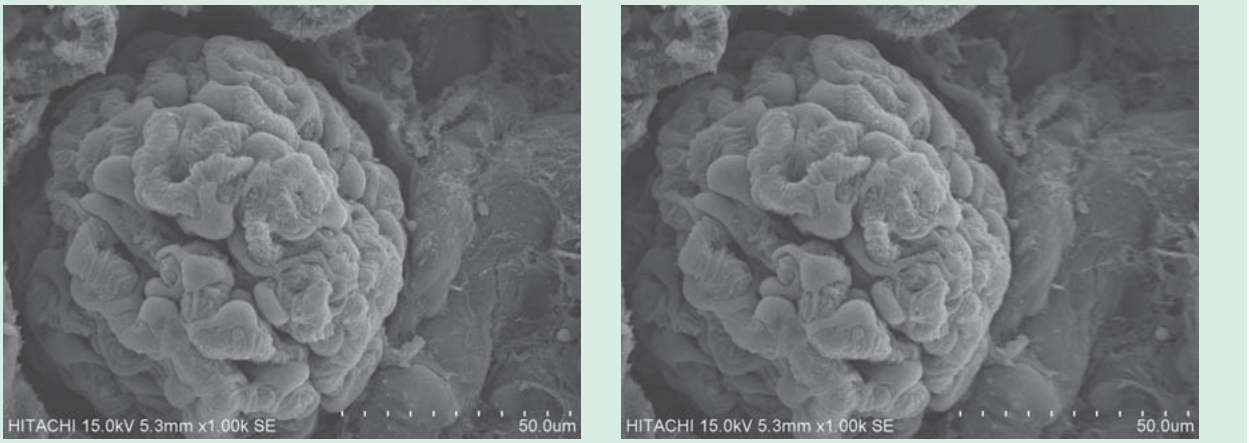


Fig. 2—Stereoscopic Imaging Using Electron Beam Tilting.
The figure shows how the tilt angle control coil (which is different from the deflecting coil used for scanning) is incorporated above the objective lens. This tilt angle control coil is used to tilt the angle of the electron beam left and right for each line.



3D: three dimensional

Fig. 3—Stereoscopic Images Obtained by Electron Beam Tilting (Glomerulus from Rat Kidney).
These images can provide a 3D image when viewed using the cross-eyed method. Electron Beam Tilting is a practical technique for viewing at low magnification.

lens to obtain the two stereoscopic images, the electron beam needs to be directed through the lens at a point away from the center (off-axis). This tends to result in a loss of resolution due to the aberrations associated with electron beam tilting.

The resolution, R_{eso}, when using electron beam tilting can be calculated using the following formula (mean squares method).

$$R_{eso} = \sqrt{\Delta W_{S0}^2 + \Delta W_{RL}^2 + \Delta W_{C1}^2 + \Delta W_{C0}^2 + r_d^2 + (r_{SS})^2} \qquad (1)$$

Here, ΔW_{S0} = spherical aberration, ΔW_{RL} = comatic aberration, ΔW_{C1} = off-axial chromatic aberration (sum of chromatic aberration due to magnification and rotation), ΔW_{C0} = axial chromatic aberration, r_d = diffraction aberration, and r_{SS} = light source diameter on sample.

Using this formula to analyze the relationship between the electron beam tilting angle and the resolution on a general-purpose SEM, consisting of a thermal-electron gun electron source and out-lens, indicates that the fall in resolution when electron beam tilting is used is due to the off-axial aberrations (comatic aberration and off-axial chromatic aberration) (see Fig. 4). Spherical aberration, axial chromatic aberration, and diffraction aberration are all independent of the electron beam tilting angle and are present even when $t1 = 0°$. Accordingly, they are omitted from the diagram because they have little influence on the loss of resolution when using electron beam tilting. Furthermore, because astigmatism can be reduced using the stigmator that is typically provided on general-purpose SEMs, it is not included when considering resolution for electron beam tilting.

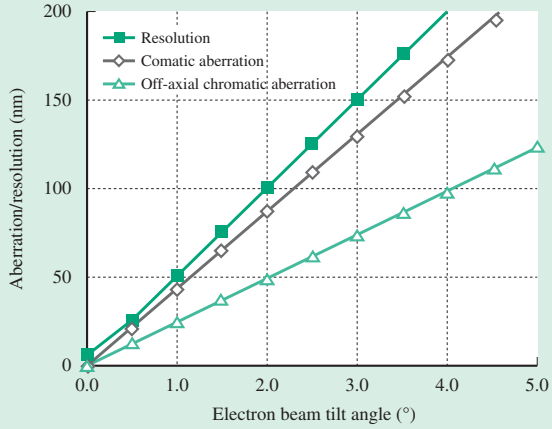


Fig. 4—Relationship between Electron Beam Tilting Angle and Resolution.
Tilting the electron beam degrades the resolution due to comatic aberration and off-axial chromatic aberration.

This indicates that the resolution for electron beam tilting at an angle of 3°, for example, will fall to approximately 150 nm. This is equivalent to a magnification of about ×2,000, indicating that blurring can be anticipated when the technique is used at any higher magnification. Despite this, an instrument capable of 3D imaging with realtime stereo display at low magnification and conventional SEM operation at high magnification would still be useful. This was the thinking behind the development of SEM SU3500 (see Fig. 5).

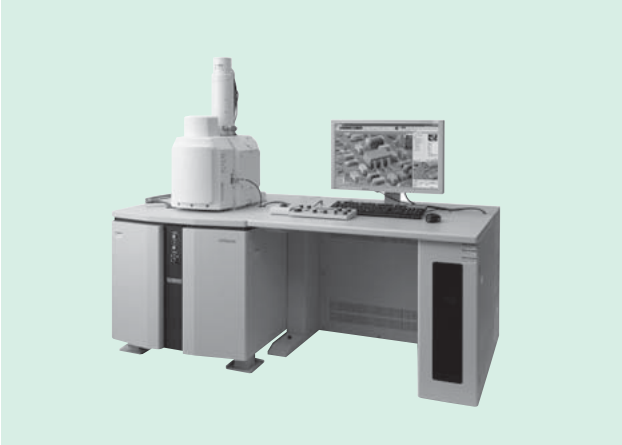


Fig. 5—SEM SU3500.
This SEM uses electron beam tilting to provide realtime stereoscopic imaging.

Development of Optics with Low Aberration

Nevertheless, achieving high resolution on a realtime stereo SEM is an essential step in the development and practicality of the instrument. Accordingly, to enable 3D imaging at high magnifications, we investigated ways of reducing aberrations due to the use of electron beam tilting[5), 6)]. Specifically, a lens that reduces aberration due to electron beam tilting (aberration reduction lens) was added on the electron source side (relative to the objective lens), and steps were taken to reduce aberration due to the objective lens (see Fig. 6).

Incorporation of this aberration reduction lens into the optics of the realtime stereo SEM was shown to provide a marked improvement in the resolution of the two stereoscopic images. For example, the modified optics can achieve a resolution of 15 nm at a tilt of 3°, which means that observations can be made with magnifications of ×20,000.

ADVANCES AND INNOVATIONS IN 3D IMAGING TECHNIQUES

The ability of the realtime stereo SEM to obtain the two stereoscopic images simultaneously meant that there was a need to investigate techniques that would enable it to be used for simple on-screen 3D imaging. Numerous techniques exist for 3D imaging and the following two were identified as being suitable for the realtime stereo SEM and for a wide range of applications. The commercial models of the realtime stereo SEM can use either of these techniques.

Viewing through 3D Glasses

The easiest and most widely applicable technique is to display the left and right stereoscopic images in red and blue, overlaid on each other, and to view them through 3D glasses with red and blue color filters (cellophane) covering the respective lenses. This technique is called anaglyph 3D. Because the

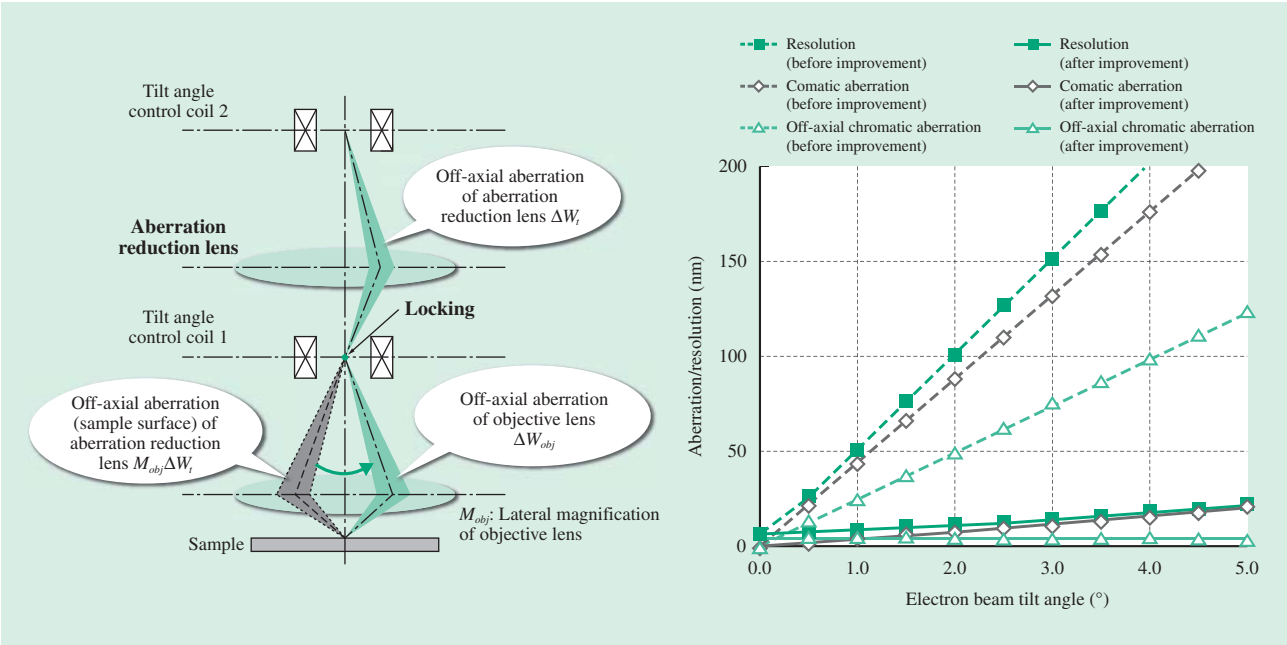


Fig. 6—Conceptual Diagram of Optics with Low Aberration.
The aberration in the objective lens when using electron beam tilting is canceled out by using the aberration reduction lens to induce an aberration that is symmetrical with respect to the optical axis.

effect is easy to produce on a PC screen, a realtime stereo SEM display screen can use anaglyph images to enable realtime TV-rate 3D viewing. Another advantage is that, if the two stereoscopic images are stored as anaglyph images, they can be viewed on a conventional projector or monitor by viewers wearing the 3D glasses. Accordingly, this is provided as a standard function on the commercial models of the realtime stereo SEM.

Another technique is to project the left and right images using light of different polarization and to view them through glasses with polarized filters. This can be done using either circularly or linearly polarized light. With this technique, 3D images from the SEM can be viewed in realtime by displaying the two stereoscopic images on a special-purpose monitor.

Naked-eye Viewing on Special-purpose 3D Liquid Crystal Display Monitor

Naked-eye 3D displays are a recent development that allow people to view 3D images without the need for the 3D glasses referred to above. This is frequently achieved either with a parallax barrier method or a lenticular method. The former separates the images delivered to the left and right eyes by placing a filter in the form of vertical or horizontal stripes on top of the image whereas the latter achieves this using a sheet of small lenses. However, because both methods require the light to pass through a filter, they still suffer from problems such as moiré patterns and loss of brightness. Furthermore, because the left and right images are displayed on the same monitor, the effect is to halve the monitor resolution.

In response, naked-eye 3D monitors with high resolution have been developed that are suitable for displaying images from the realtime stereo SEM.

MANIPULATION USING REALTIME STEREO SEM

We believe that this ability to perform realtime 3D imaging using an SEM is starting to bring major changes to the field of scanning electron microscopy. While there have been attempts in the past to manipulate samples inside an SEM, for example, because it has only been possible to work with monocular images on previous SEMs, these have struck difficulties when performing delicate operations because of the lack of depth perception provided by the image. The task can be likened to trying to thread a needle with only one eye open. When manipulating a sample in a realtime stereo SEM, by contrast, it is possible to obtain an accurate 3D view of the positional relationship between the sample and a tool (such as a dissection needle).

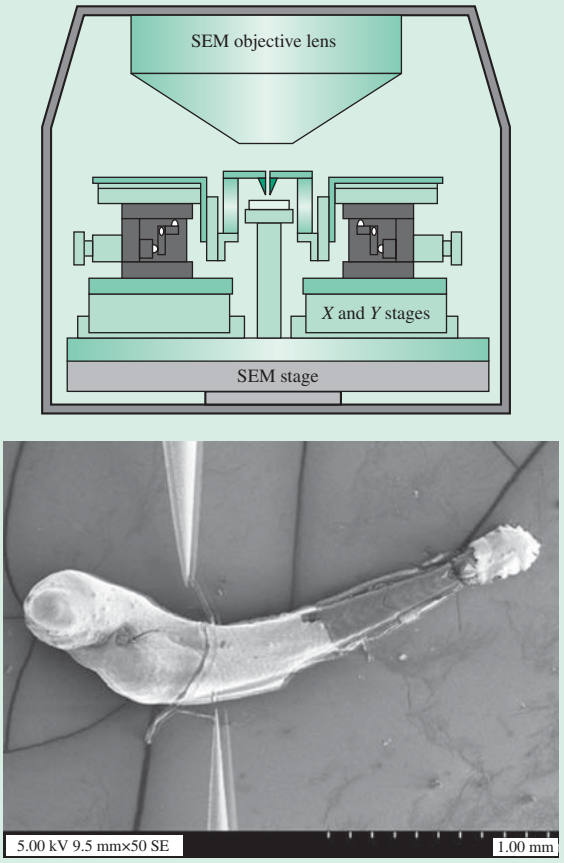


Fig. 7—Conceptual Diagram of Micro-manipulator in SEM Sample Chamber (top) and Image of Its Use for Microanatomical Dissection of Zebra Fish Embryo (bottom). The image at the bottom is the anaglyph overlay of two stereoscopic images.

Accordingly, we have demonstrated the usefulness of the realtime stereo SEM by developing a micro-manipulator that can be fitted on the microscope and used to manipulate biological samples or perform microdissections[7), 8)].

To achieve this, a prototype of the micro-manipulator was built that was able to be placed inside the SEM sample chamber and operated remotely. This micro-manipulator can be used to perform a variety of tasks or operations on the sample inside the SEM while using 3D imaging to view it in realtime. It is also possible to operate tools such as a dissection needle or tweezers with two hands by installing a number of these manipulators in the SEM sample chamber (see Fig. 7). Operations that can be performed in this

way include using a dissection needle to remove a glomerulus (an agglomeration of blood vessels found in the kidney) from a sample and place it in a desired location, or to detach fibers from the lens of the eye.

By combining the micro-manipulator with a tactile feedback system using a haptic device, it is also possible for the operator to feel things like undulations on the surface of the sample or the force on the needle as they work. By incorporating additional techniques for sample preparation, there is also potential for providing the ability to perform actions under an SEM in much the same way as performing a dissection by hand under a stereoscopic microscope.

CONCLUSIONS

This article has explained the principles of operation and basic design of a realtime stereo SEM that was developed to take greater advantage of the characteristics that make SEMs suitable for viewing 3D structures, and has described how manipulation can be performed inside the SEM when it is used in biology.

Technical innovations in recent years have led to major advances in 3D imaging that are already making their presence felt in movies, television, and other areas of popular culture. Given the steady stream of new 3D electronic devices appearing on the market, such as digital cameras, TVs, personal computers, and mobile phones, the development of a realtime stereo SEM is very much in step with the times. Nevertheless, it will be extremely gratifying if this development is able to give a boost to the field of scanning electron microscopy and to be adopted in a wide range of applications. This development has the potential to open up the world of scanning electron microscopy that is different in so many ways from that of transmission electron microscopes.

ACKNOWLEDGMENTS

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Featured Articles

Easy-to-use Atmospheric-pressure Scanning Electron Microscope for Food, Plants, and Tissue

—AE1500 Tabletop Atmospheric SEM—

Yusuke Ominami, Dr. Eng.
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Akiko Hisada
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Kenichi Sato
Sukehiro Ito

OVERVIEW: Hitachi High-Technologies developed the AE1500, a tabletop atmospheric SEM that is capable of scanning electron microscopy under atmospheric pressure, by using a membrane that allows an electron beam to pass while keeping the atmospheric-pressure chamber and evacuated column separate. Because the specimen does not come into contact with the membrane, a feature of the AE1500 is its ability to observe bulk specimens under atmospheric pressure. Hitachi High-Technologies also developed the ES-Corrector algorithm to correct the image for the electron beam scattering that occurs due to the presence of atmospheric gases between the membrane and the specimen. This means that bulk, high-moisture specimens such as food or biological samples can be observed with the electron microscope under atmospheric pressure without preprocessing.

INTRODUCTION

SCANNING electron microscopes (SEMs) (which are used to observe microscopic features) have become essential tools in numerous different areas of research and development. The specimen chamber of an SEM is typically maintained at a pressure between 10^{-5} Pa (hard vacuum) and 10^{2} Pa (soft vacuum). This is done to keep the path of the electron beam free of gases because of the scattering that occurs when electrons collide with gas molecules. On the other hand, there is strong demand for the use of SEMs for high-magnification observations of tissue and other soft materials that contain water. Unfortunately, because the saturated vapor pressure of water at room temperature is only about 2.3×10^{3} Pa (2.3 kPa), it is difficult to observe specimens in a hydrated state using a conventional SEM because evaporation occurs even when used with a soft vacuum of 10^{2} Pa. While SEM observations under atmospheric pressure have previously been reported in the literature, their use has been subject to restrictions.

In response, Hitachi High-Technologies Corporation has developed a tabletop SEM that is easy to use for observation of water-containing specimens under atmospheric pressure. This article describes the AE1500 tabletop atmospheric scanning electron microscope.

BACKGROUND

A number of methods for making SEM observations of a specimen under atmospheric pressure have previously been reported in the literature[(1) – (3)]. Most of these have exposed the specimen to the electron beam via a very thin membrane (tens of nanometers) that keeps evacuated column and atmospheric-pressure chamber separate, but in doing so, have required the specimen to be placed on the membrane [see Fig. 1 (a)].

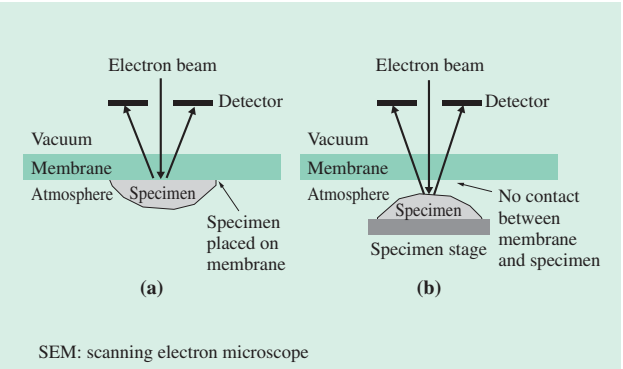


Fig. 1—Techniques for Atmospheric SEM Imaging.
The observation of bulk material is difficult when the membrane and the specimen are in contact as in diagram (a). When there is no contact between the membrane and the specimen, as in diagram (b), the observation of bulk material is easy, however the electron beam is scattered by the intervening gas molecules.

The problem with this approach is that it makes it difficult to observe bulk materials such as food, plants, or biological tissue.

In response, Hitachi High-Technologies has devised a technique for SEM observation under atmospheric pressure in which the specimen is placed on a stage, thereby avoiding any contact with the membrane [see Fig. 1 (b)][4]. Although this makes it easy to observe bulk materials, it has been assumed in the past that this will make SEM imaging impossible because the separation between the membrane and the specimen results in electron beam scattering due to the gas molecules in the atmosphere. However, by going back to the principles behind electron beam scattering, Hitachi High-Technologies determined that SEM images can be obtained even when there is a degree of separation between the membrane and the specimen. Hitachi High-Technologies has also developed the ES-Corrector image enhancement technique (which corrects for electron beam scattering) to produce crisp SEM images from which the effects of electron beam scattering have been removed.

The following section describes the design and features of the atmospheric SEM, and the techniques that make it possible to perform SEM observations under atmospheric pressure.

MICROSCOPE AND ASSOCIATED TECHNOLOGY

Microscope Concept and Technical Challenges

The objective in developing the atmospheric SEM was to enable everyday items to be examined under atmospheric pressure in such fields as food, agriculture, pharmaceuticals, and medicine.

Fig. 2—AE1500 SEM.
The AE1500 went on sale in September 2015.

Hitachi High-Technologies has been selling its TM3030 tabletop SEM internationally since 2010. As the TM3030 can be placed on a desk, it is used in a wide range of fields, including things like science education for children as well as research and development, and industrial applications. The AE1500 tabletop atmospheric SEM was developed based on the TM3030, the latest tabletop model, and came about out of a desire to make an atmospheric SEM that would be easy to use for observing everyday items (see Fig. 2).

Microscope Design

Fig. 3 shows the internal structure of the AE1500. Inside the part of the microscope that is in a state of vacuum is a chamber that can be kept under atmospheric pressure [see Fig. 3 (a)]. The specimen is placed in this atmospheric-pressure chamber. The membrane that separates the evacuated column from the atmospheric-pressure chamber is located at the top of this chamber. This allows the specimen to remain under atmospheric pressure (1 atmosphere = approximately 101 kPa) while the vacuum is maintained throughout the rest of the SEM.

The membrane (thickness: 20 nm) used for this purpose is made of silicon nitride (SiN_x), with electron beam scattering being one of the considerations behind this choice of thickness, as explained below.

The electron beam acceleration voltage is 15 kV. The electron beam is emitted by an electron gun located in the part labeled “SEM” in Fig. 3 and is focused on the specimen by an objective lens. After passing through the membrane and being scattered by atmospheric gas molecules, the electron beam reaches the specimen with an energy of approximately 15 kV. Because of the high energy of the electrons backscattered (reflected) from the specimen, they pass through the region of atmosphere and the membrane again to the backscattered electron detector. This design allows SEM observation under atmospheric pressure.

The specimen is aligned under the membrane by placing it on a holder and then inserting the specimen stage into the chamber [see Fig. 3 (b)]. Using its vacuum pump, the microscope is able to create a negative pressure around the specimen (ranging from a few kPa up to 101 kPa, corresponding to between 0.1 and 1 atmosphere) [see Fig 3 (c)]. Similarly, soft vacuum SEM observation (ranging between a few Pa and several tens of Pa) can also be performed by removing the membrane [see Fig 3 (d)].

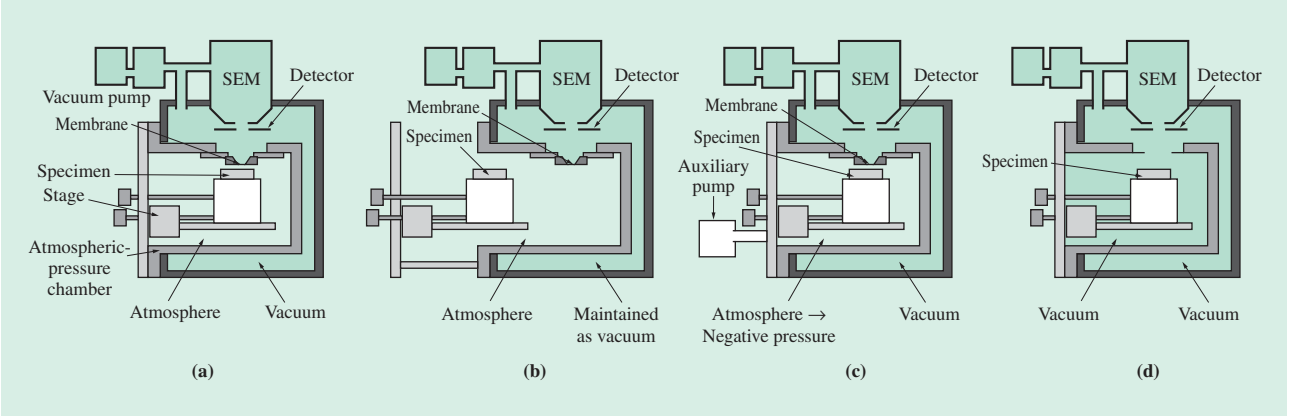


Fig. 3—Internal Structure of AE1500.
Diagram (a) shows SEM observation under atmospheric pressure (101 kPa), (b) shows specimen insertion, (c) shows SEM observation with negative pressure (from several kPa to 101 kPa), and (d) shows vacuum SEM observation (several Pa to several tens of Pa). The AE1500 supports all of these different SEM observation modes: atmospheric pressure, negative pressure, and vacuum. Although not shown in the diagrams, the electron beam is generated by an electron gun and focused on the specimen by an objective lens in the SEM unit.

Electron Beam Scattering

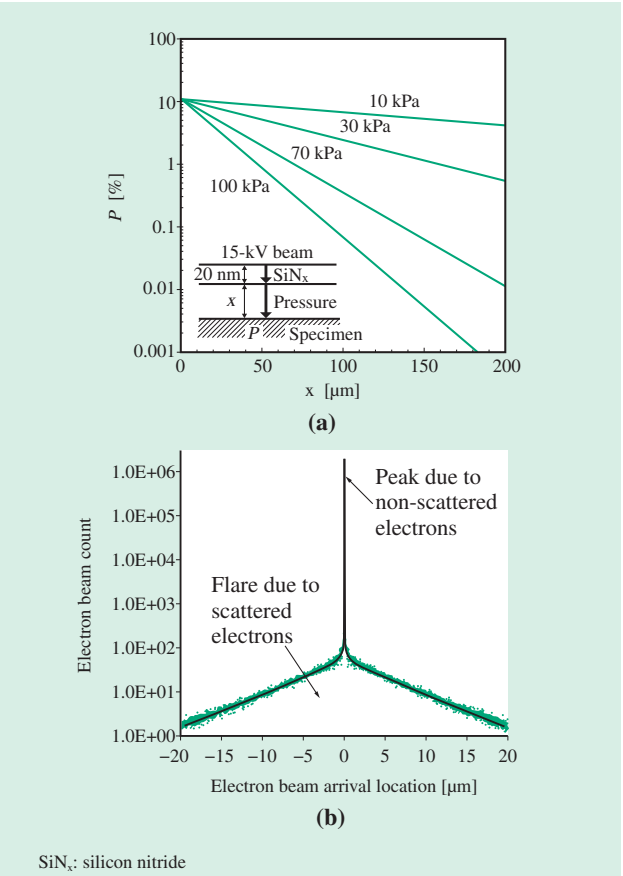
The distance between the membrane and the specimen in the new atmospheric SEM means that electron beam scattering due to atmospheric gases will invariably occur. As it was believed that this would make SEM images difficult to obtain, most atmospheric SEMs reported to date have used the technique in Fig. 1 (a). However, by going back to the principles behind electron beam scattering, Hitachi High-Technologies determined that SEM images can be obtained even when there is a degree of separation between the membrane and specimen. The following explains how.

An electron beam that passes through an atmosphere is scattered by the gas molecules. A certain proportion of the electrons, however, will not collide with any atmospheric gases stochastically and so will not be scattered. These are referred to as non-scattered electrons. The proportion P of electrons that are not scattered is as follows[4].

$$P = exp\left(-\frac{N\rho\sigma}{A}x\right) \quad (1)$$

Here, N is the number of gas molecules, ρ is the density (g/cm^3), σ is the scattering cross section area (cm^2), A is the mass number, and x is the distance traveled by the electrons (cm).

Fig. 4 (a) shows the proportion P of electrons that are not scattered after passing through the membrane (SiN_x, 20-nm thickness) with an acceleration voltage of 15 kV and traveling the distance x between the membrane and the specimen. Atmospheric pressure is 100 kPa, with the results for other pressures being



SiN_x: silicon nitride

Fig. 4—Relationship between Distance from Membrane to Specimen and Proportion of Non-scattered Electrons and Results of Beam Profile Simulation.
Graph (a) shows the relationship between the distance from membrane to specimen and the proportion of non-scattered electrons, and graph (b) shows the results of a beam profile simulation. Because some electrons reach the specimen without being scattered, even under atmospheric pressure (100 kPa), the beam profile always includes a central peak.

shown for reference. The important point to note here is that the value of *P* does not fall to zero even if the distance *x* between the membrane and the specimen is large. In other words, although the scattered electrons will end up somewhere other than the focal point targeted by the objective lens, those electrons that are not scattered will arrive at the focal point, with *P* being the proportion of such electrons.

Fig. 4 (b) shows the beam profile calculated by a Monte Carlo simulation for an electron beam with an acceleration voltage of 15-kV after passing through the membrane (SiN_x, 20-nm thickness) and traveling the 100 µm distance between the membrane and the specimen. As shown in the figure, even after passing through 100 µm of atmosphere, the beam profile has both a wide tail (flare) due to scattered electrons and a sharp peak due to non-scattered electrons. That is, the beam profile of the atmospheric SEM at the specimen is the sum of scattered (beam flare) and non-scattered (central beam) components.

Fig. 5 shows a comparison of vacuum and atmospheric SEM images of a pattern of metal on silicon (Si). Fig. 5 (a) and 5 (b) are vacuum SEM images taken under a pressure of 10 Pa, and the image in Fig. 5 (c) is an atmospheric SEM image of the same location as 5 (a) taken with a distance of 100 µm between the membrane and the specimen. At first glance, image (c) appears blurred due to scattering of the electron beam by the atmosphere. However, when the magnification of image (c) is increased at the same position as image (b) and the brightness and contrast are adjusted, the detail of the metal pattern becomes clearly recognizable [see Fig. 5 (d)]. If the image really had been blurred by scattering of the electron beam, this detail should not be visible. From this it can be concluded that blurring due to scattering of the electron beam by the atmosphere is not the correct interpretation of the phenomenon.

The reason why the detail is still visible despite atmospheric scattering is believed to be as follows. Electrons that are not scattered by atmospheric gases are concentrated at the focal point. The diameter of the central beam of non-scattered electrons is the same regardless of whether the specimen is in an atmosphere or vacuum. Accordingly, the non-scattered electron beam serves to form the same detailed image as the vacuum SEM. The scattered electron beam, by contrast, travels in many different directions, and although it worsens the image contrast, it does not play any part in forming the detailed image, and therefore does not cause blurring. This means that, as long as the central beam is sufficiently powerful, it is possible to observe details in an atmospheric SEM image even if there is a gap between the membrane and specimen.

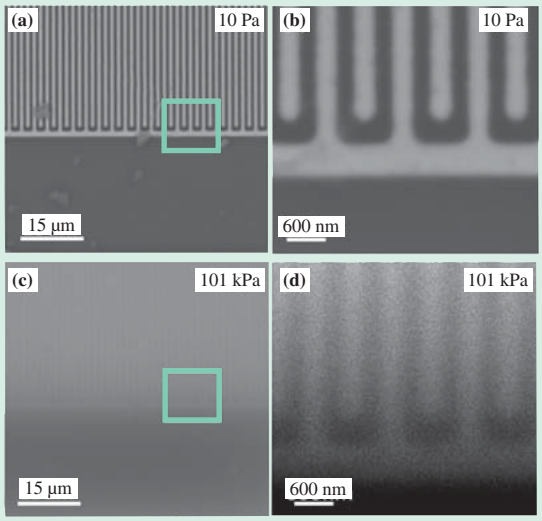


Fig. 5—Comparisons of Vacuum SEM and Atmospheric SEM Images of Metal Pattern on Si.
Images (a) and (b) show vacuum SEM images of a metal pattern at × 5 k and × 30 k magnification, respectively. Images (c) and (d) show atmospheric SEM images of the metal pattern at × 5 k and × 30 k magnification, respectively. Details of the metal pattern can be clearly identified at high magnification in the atmospheric pressure image, just as in the vacuum image.

Image Enhancement Technique

This section describes an image enhancement technique for removing the influence of the scattered electron beam from the SEM image.

Fig. 6 (a) shows an image of the digit "9" formed in metal on Si, acquired under atmospheric pressure. Although the image appears blurred, the outline of the digit is clearly visible. This is due to the non-scattered electrons. Similarly, it can be assumed that the blurred appearance of the overall image (bright area around the digit) is due to the scattered electrons.

Given this interpretation, the problem was assumed to be caused by electron beam scattering between the membrane and the specimen, and it was concluded that, in practice, this could be treated as an electron scattering (ES) field whereby the electron beam is reliably scattered in a repeatable manner (mathematically, this field can be represented by a single transfer function). Recognizing that significant image enhancement would be possible if this ES field could be determined and removed from the image,

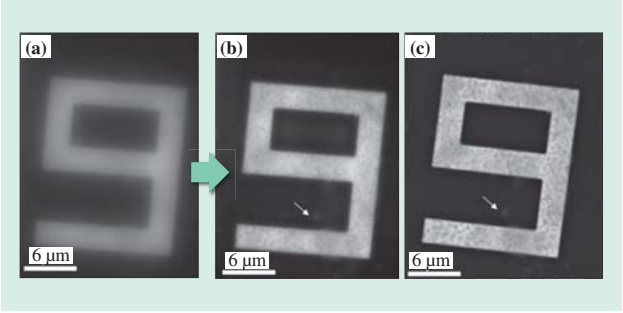


Fig. 6—Digit Formed in Copper on Si Substrate.
Image (a) shows the atmospheric SEM image of the digit "9" formed in copper on an Si substrate, image (b) shows the image after correction by the ES-Corrector image enhancement algorithm, and image (c) shows the vacuum SEM image. Image enhancement makes it possible to see the contaminant indicated by the white arrow.

Hitachi High-Technologies developed the ES-Corrector algorithm that corrects for electron beam scattering[6]. Fig. 6 (b) shows the image produced by this image enhancement algorithm and Fig. 6 (c) shows an image of the same specimen taken in vacuum. Images (b) and (c) show sub-micron details of the metal film surface, including a contaminant at the location indicated by the white arrow in the figure that is nearly invisible in image (a). This demonstrates the high level of image enhancement achieved in image (b).

Fig. 7 shows a variety of enhanced specimen images acquired under atmospheric pressure. Images (a), (b), and (c) show the original atmospheric SEM images (before correction by ES-Corrector), and images (d), (e), and (f) show the corrected images. This demonstrates the improvement in image quality that results from eliminating the effect of electron beam scattering and enhancing the contrast.

EXAMPLE OBSERVATIONS

As noted above, SEM imaging of specimens under atmospheric pressure can be performed even when there is a gap (no contact) between the membrane and the specimen. The advantage of this technique is that it can be used to observe bulk materials such as food, plants, or biological tissue simply by placing the specimen on the stage. The following describe examples of such observations.

(1) Observation of food

By removing the membrane from the AE1500 and changing from the configuration shown in Fig. 3 (a) to that in 3 (d), a specimen viewed under atmospheric pressure can also be viewed in vacuum. Fig. 8 shows two images of the same location on the surface of dried pasta taken under atmospheric pressure and in vacuum respectively. Whereas the starch grains of the pasta are visible in image (a), the vacuum image in (b) includes a large number of cracks that are not visible in image (a). This indicates how exposure to vacuum can result in cracking even in an already dry specimen. From this, it can be concluded that specimens that

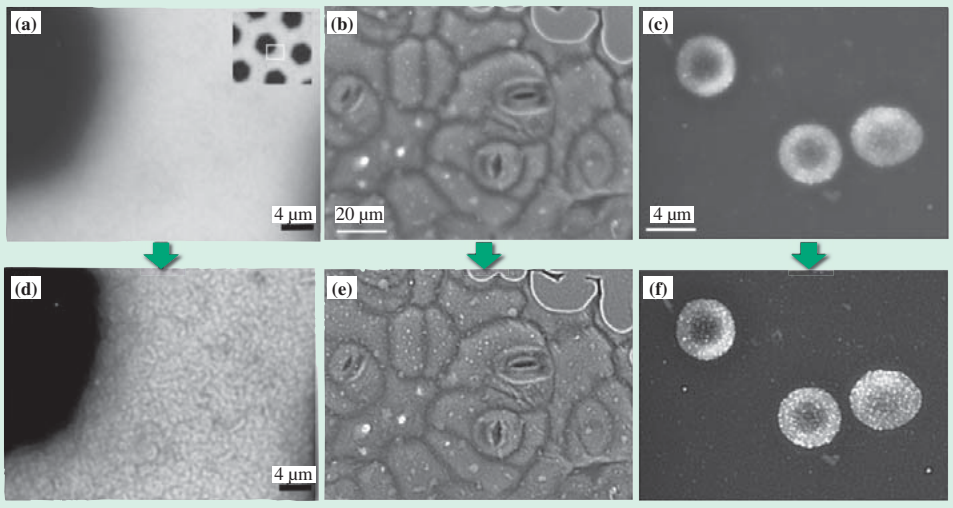


Fig. 7—Image Enhancement of Specimen Observed under Atmospheric Pressure.
Image (a) shows a copper mesh, (b) a daikon radish leaf, and (c) the red blood cell of a rat immunostained with colloidal gold. The images were obtained with an acceleration voltage of 15 kV, at room temperature, and at one atmosphere.

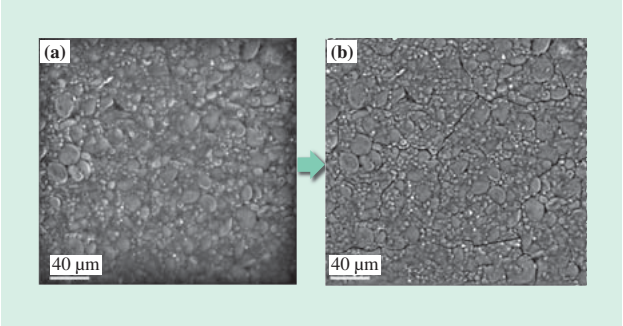


Fig. 8—Observation of Dried Pasta.
Image (a) shows a surface image of dried pasta under atmospheric pressure, and image (b) shows a surface image taken in vacuum. As cracking occurs even in a dry specimen exposed to vacuum, it is preferable that specimens containing even a small amount of moisture be observed under atmospheric pressure.

potentially contain water are better observed under atmospheric pressure.

(2) Observation of cosmetics drying process

Fig. 9 shows images of sunscreen used to protect the skin against ultraviolet rays. Sunscreen contains silica, titanium, or other fine particles suspended in a fluid. Atmospheric pressure observations were made of the drying of sunscreen applied to a substrate. The images show how the large quantity of water or other liquid present at 30 seconds after application has largely evaporated after 5 minutes, and is almost entirely dry after 15 minutes, leaving large numbers of residual fine particles adhering to the substrate. This behavior of fluid on a substrate was something that could not be observed using conventional vacuum SEM. It is also common in the case of cosmetic, pharmaceutical, and other similar observations that drying of the substrate (such as skin) must be avoided as well as that of the liquid specimen. Achieving this requires that SEM observations be made under atmospheric pressure.

(3) Observation of tissue

This example involves the observation of animal tissue[5]. A scalpel was used to cut the large intestine from the gastrointestinal tract of a rat fixed in formalin [see Fig. 10 (a) and (b)] and the intestinal cross section was viewed using a stereoscopic optical microscope [see Fig. 10 (c)]. The same cross section was then viewed using the AE1500 without preprocessing such as staining or vapor deposition [see Fig. 10 (d)]. Fine details that are not visible through the stereoscopic microscope can be clearly observed using the AE1500. Next, the SEM specimen was dehydrated, embedded in paraffin, sliced, the paraffin was removed, and then specimen was stained with hematoxylin and eosin (H&E), a standard practice for preparing thin-slice tissue specimens. The image of the resulting specimen viewed through a biological microscope is shown in Fig. 10 (e). Features such as intestinal villi are clearly visible, demonstrating that the process of atmospheric SEM observation preserved the state of the tissue without drying out the specimen.

The reason why fine details could not be seen using the stereoscopic microscope is because of the strong tendency for light to pass directly through the specimen, so that rather than only showing the surface structure, images of the interior are also superimposed on the result. The usual way to make these details visible is to first slice and stain the specimen as in Fig. 10 (e). The problem with this is that procedures like embedding and slicing require a lot of work. Atmospheric SEM involves the detection of electrons that are backscattered from the surface, with the

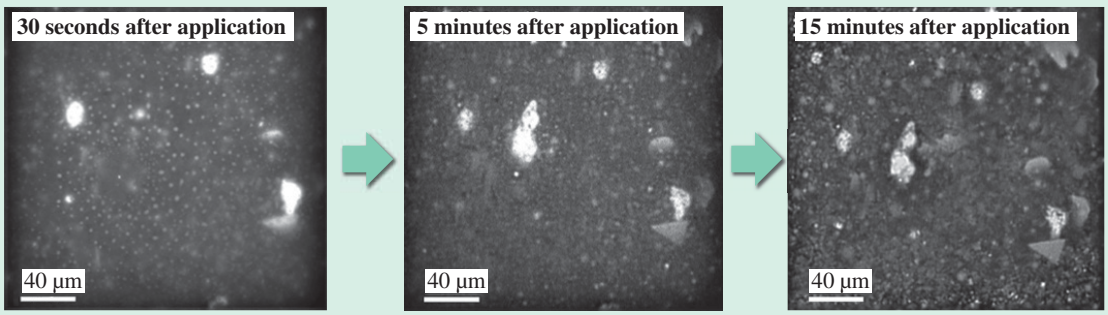


Fig. 9—Observation of Cosmetic in the Process of Drying.
The drying of liquid sunscreen is evident 30 seconds after application, together with the deposition of the fine particles contained in the sunscreen. The image after 15 minutes shows that drying is complete and fine particles have adhered to the substrate.

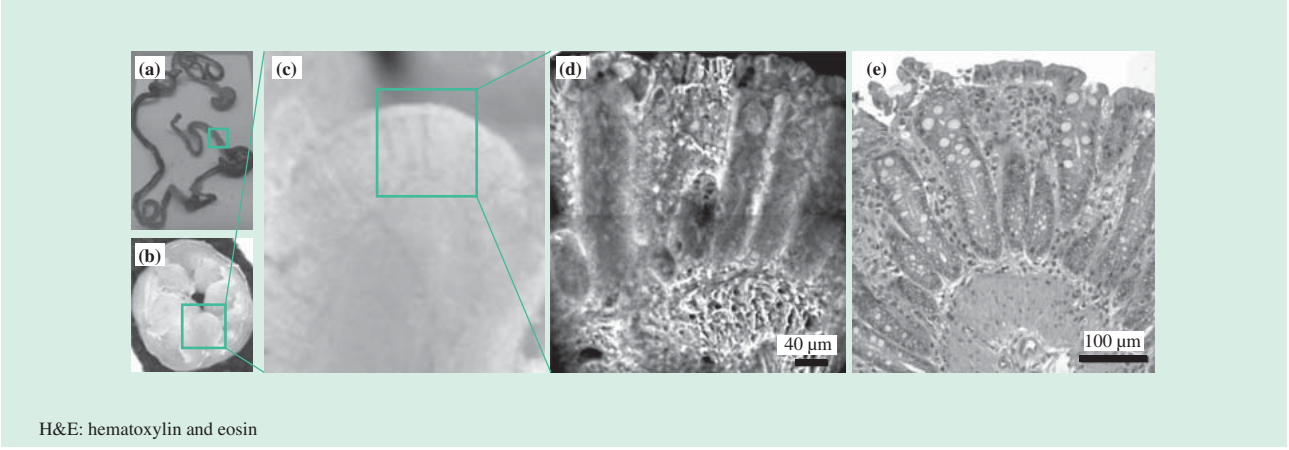


Fig. 10—Images of Rat Intestine.
Image (a) is a gastrointestinal tract that has been removed from a rat, (b) is a cross section of its large intestine, (c) is a stereoscopic microscope image, (d) is an atmospheric SEM image, and (e) is a biological microscope image taken after the specimen was preserved in paraffin, sliced, and stained with H&E. The atmospheric SEM can obtain information about the fine structures on the surface of tissue without preprocessing.

electron beam by its nature not passing through the specimen. In other words, it is a more sensitive way of observing surfaces than optical microscopy. This is why atmospheric SEM can view fine details that are not visible by a stereoscopic microscope that uses light [see Fig. 10 (d)]. The use of atmospheric SEMs to obtain information about fine details and identify suitable samples prior to preparations such as embedding the tissue in resin or slicing it has the potential to be a very useful technique for the examination of tissue samples.

CONCLUSIONS

Hitachi High-Technologies found that an SEM image could be obtained from the non-scattered electrons even when the membrane and specimen are not in contact and atmospheric gas molecules are present in the electron beam path. Hitachi High-Technologies also developed the ES-Corrector algorithm for electron beam scattering correction that can remove the effect of electron beam scattering from atmospheric SEM images and demonstrated that this significantly enhanced atmospheric SEM images. By making it possible to view specimens under atmospheric pressure, which in the past could only be viewed in vacuum, SEM observations can now be made of solid water-containing specimens without preprocessing.

It is anticipated that this will contribute in the future to fields where little use has been made of SEMs in the past, such as food, cosmetics, pharmaceuticals, and medicine.

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Featured Articles

Nanoscale Imaging, Material Removal and Deposition for Fabrication of Cutting-edge Semiconductor Devices

—Ion-beam-based Photomask Defect Repair Technology—

Anto Yasaka, Ph.D.
Fumio Aramaki
Tomokazu Kozakai
Osamu Matsuda

OVERVIEW: FIB technology is applied to repair defects in lithography photomasks used in semiconductor device fabrication. Cutting-edge devices demand nanometer-scale minimum processing dimensions and precision for defect repair. To meet these scaling requirements, Hitachi has developed a novel gas field ion source. This breakthrough scaling technology replaces liquid metal ion sources, an area in which Hitachi has over 30 years of experience. It has been implemented into a defect repair system to confirm that it satisfies cutting-edge performance requirements such as minimum processing dimension, repair precision, and post-repair photomask optical properties.

INTRODUCTION

LITHOGRAPHY technology helps enable higher integration of semiconductor devices. It uses reduction projection exposure to repeatedly print the circuit pattern on a photomask onto a wafer. It is therefore vital that the photomask (which can be considered the circuit pattern original) be free of defects during semiconductor device fabrication. Since cutting-edge device pattern dimensions are scaled down to 20 nm or less, defect sizes on problem photomasks are also of a nanometer scale, and the defect repair technology must also be scaled.

A system using a focused ion beam (FIB) was developed to repair photomask defects. Over the 30 years since the release of the first unit in 1985, this technology has been used to repair defects in photomasks for ever more advanced cutting-edge semiconductor devices, helping improve semiconductor fabrication yields. The following describes the FIB-based photomask defect measurement/repair technology and the latest developments in this area.

FIB-BASED DEFECT MEASUREMENT/ REPAIR TECHNOLOGY

FIB technology was perfected in the early 1980s with the development of liquid metal ion sources, and subsequently came into widespread use. A major feature of FIB technology is its ability to achieve a small beam spot of 1 μm or less in diameter. By scanning a sample with an ion beam, the technology can be used as a scanning ion microscope, replacing the electrons of a scanning electron microscope (SEM) with ions. Moreover, using ion beam-based sputtering effects and surface reactions enables minute processing for localized etching and deposition. In other words, a single beam has three functions: imaging, material removal and deposition. These functions are used to implement photomask defect measurement and repair.

FIB-based Photomask Defect Repair System

Fig. 1 shows the composition of an FIB defect repair system. The major components include a high-brightness ion source, an ion optics system used to focus the ion beam on a minute spot and scan it, a charged particle detector used for ion image acquisition, an electron gun used to neutralize the charge on the photomask surface, a material gas injection system for localized etching and deposition, an XY stage used to mount and move the photomask, a vacuum evacuation system, and a mask transport system.

The general procedure for measuring/repairing photomask defects is as follows:

(1) Use defect coordinate data from the defect inspection device to move to the defect location.

(2) Acquire the scanned ion image of the area containing the defect.

(3) In the scanned ion image, determine the repair area

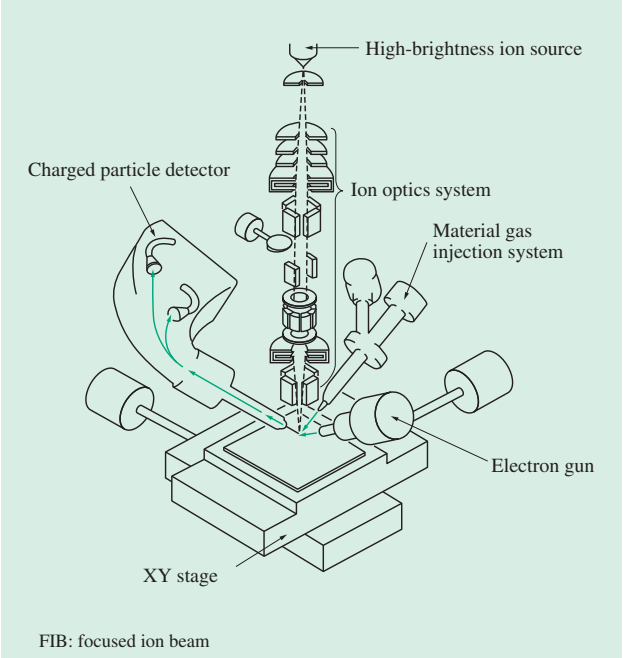


Fig. 1—Composition of FIB-based Defect Repair System. This schematic diagram shows the relationships of the components placed in a vacuum.

and method according to the type of defect.
(4) Repair the defect by locally irradiating the photomask with the FIB while injecting gas.

Fig. 2 illustrates this defect repair procedure. Photomask defects can be classified into two types, (a) excess film defects caused by residual pattern film, and (b) missing film defects caused by lacking pattern film. Type (a) defects are called opaque defects since they block light, and type (b) defects are called clear defects since they allow light to pass through. The type of repair done depends on the defect type (opaque or clear). Opaque defects are repaired by etching done to remove the excess film, and clear defects by depositing material onto the area of missing film.

Performance Demanded of Cutting-edge Photomask Defect Repair Technology

As semiconductor devices become increasingly integrated, the following three capabilities are continually demanded for photomask defect repair:
(1) Support for narrow line widths
(2) Improved repair precision
(3) No change in the quality of the optical properties of photomask repair areas relative to normal areas

Defect repair technology for photomasks for cutting-edge devices needs to be able to handle narrow line-width patterns of 20 nm or less, and minimum repair dimensions of 10 nm or less. The shorter wavelengths and shorter focus depths of today's lithographs create a need for very high repair precision, with reproducibility of 2 or 3 nm or less. Moreover, variations in the print dimensions of the repaired area caused by light transmittance or exposure focal-point drift need to be the same as for the normal (unrepaired) areas.

Major advances have been made in FIB technology to satisfy these demands. The following presents the technology used in the latest systems, and describes its performance.

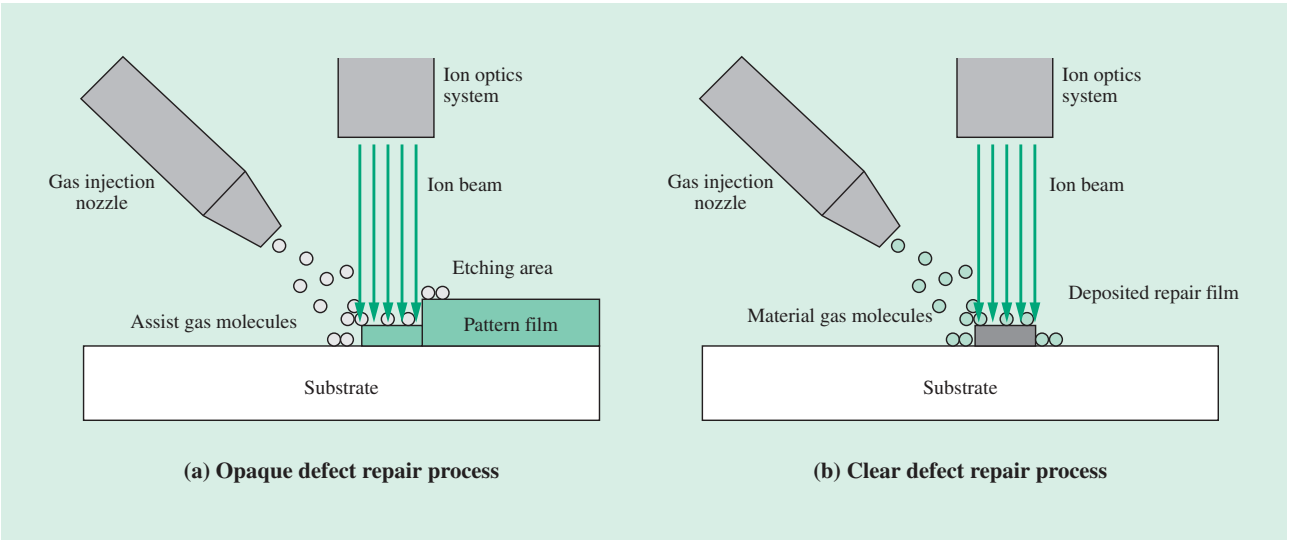


Fig. 2—Schematic Diagrams of FIB-based Defect Repair Procedures.
(a) is a schematic diagram showing the localized etching procedure for repairing opaque defects. (b) is a schematic diagram showing the localized deposition procedure for repairing clear defects.

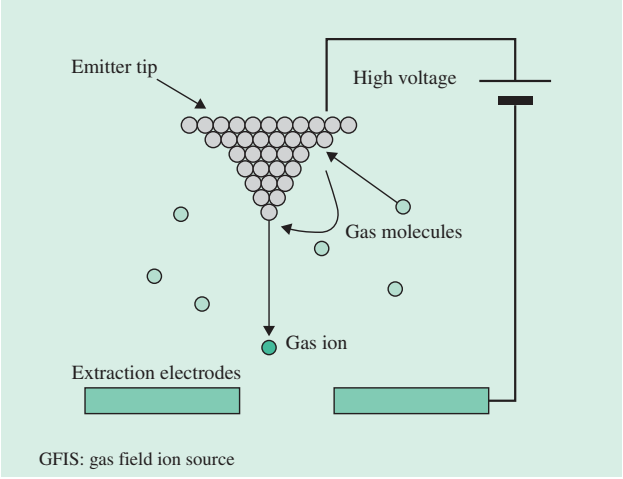


Fig. 3—Schematic Diagram of GFIS Structure.
A GFIS applies a high voltage between an emitter tip sharpened to the atomic level and opposing extraction electrodes to ionize gas molecules in the high electric field at the end of the tip.

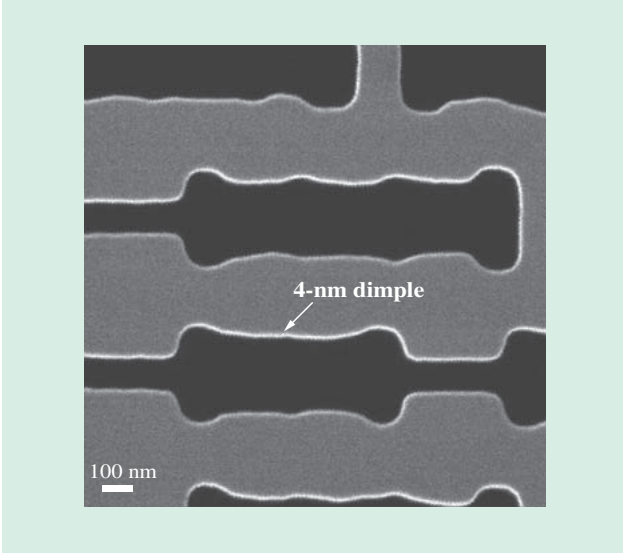


Fig. 4—Scanning Ion Microscope Image of Photomask Acquired by FIB System with GFIS Built-in.
The photo shows the image acquired by scanning a 25-keVN_2^+ beam on a photomask and detecting secondary electrons. A 4-nm defect is visible on the photomask.

OVERVIEW OF LATEST SYSTEM, PERFORMANCE EVALUATION RESULTS

System Overview

Hitachi's latest FIB defect repair system (GR3000) uses a new gas field ion source (GFIS) in place of the liquid metal ion sources Hitachi had worked with for over 30 years[1), 2)]. The GFIS applies a high voltage to an emitter tip sharpened to the atomic level, forming a strong electric field at the tip, which is used to ionize gas molecules (see Fig. 3). As ionization occurs only in the strong electric field at the tip, the ion generation area is extremely small (only a few nanometers in size), making the energy distribution of the emitted ions very narrow. The system therefore has an outstanding capability to form ion beams with small spot diameters.

Mounting the GFIS reduces the ion beam spot diameter by at least 50% relative to conventional technology, improves the scanning ion microscope image resolution, and improves the visibility of minute defects. Fig. 4 shows an example scanning ion microscope image in which a defect of 4 nm in size is visible[2)]. GFIS enables a repair process with a minimum dimension of 10 nm or less (see Fig. 5)[2)]. Since the ion species has been changed from conventional metal ions to gas molecular ions such as nitrogen or hydrogen ions, there is a major improvement in the reduction of light transmittance caused by ion implantation, which is a problem when irradiating the quartz glass that photomask substrates are made of[2), 3)].

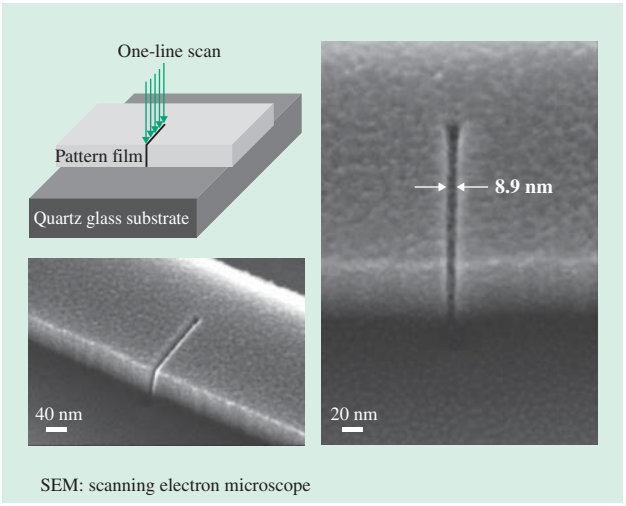
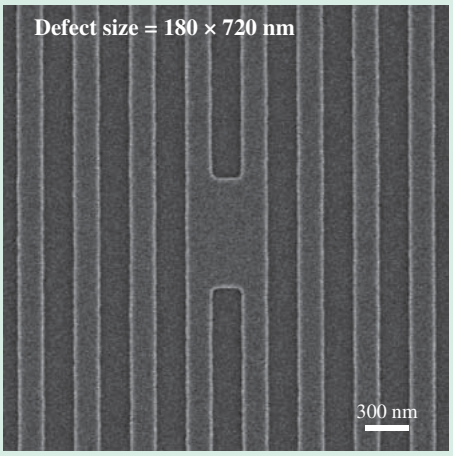


Fig. 5—Minimum Processing Dimension of GR3000.
A photomask pattern film that was line-processed with an ion beam was observed with an SEM.

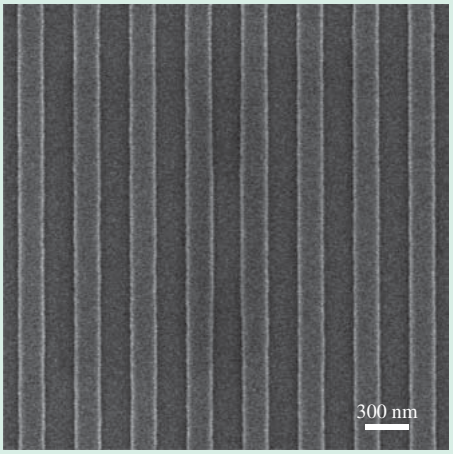
Defect Repair Performance Evaluation Results

Fig. 6 shows an example of opaque defect repair by the GR3000. It shows the before and after SEM images for repair done by using etching to remove excess film from a bridging defect in a line and space pattern on a photomask. The pattern film is made of a molybdenum and silicon (MoSiON) compound phase shift mask*.

* Phase shift mask: A photomask that controls the phase and transmittance of light to improve characteristics during exposure and to improve resolution by drawing on the phenomenon of light interference.



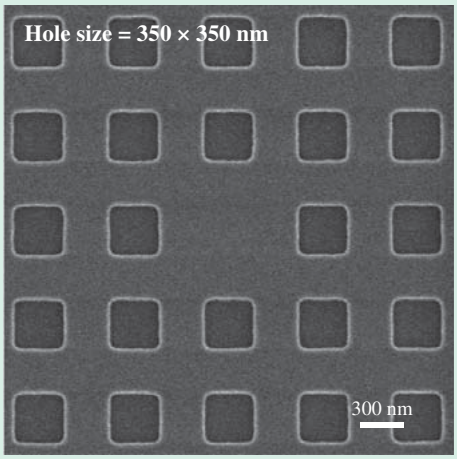
Before repair (3.0-µm field of view)



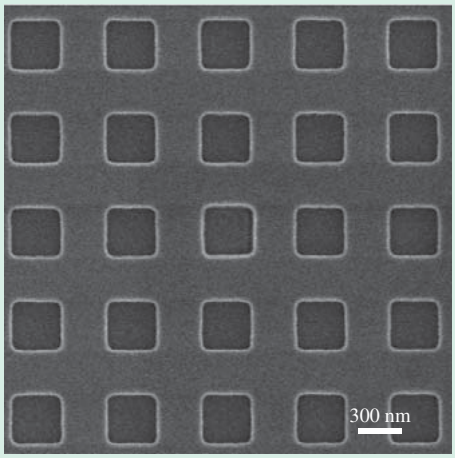
After repair (3.0-µm field of view)

MoSiON: molybdenum and silicon

Fig. 6—Example of Photomask Opaque Defect Repair Using GR3000 (Line and Space Pattern).
The photos show SEM images of the photomask before and after the repair. The pattern film is an MoSiON pattern film with a line width of 180 nm.



Before repair



After repair

Fig. 7—Example of Photomask Opaque Defect Repair Using GR3000 (Hole Pattern).
The photos show SEM images of the photomask before and after the repair. The pattern film is an MoSiON pattern film with a hole width of 350 nm.

A 25-keV nitrogen ion (N_2^+) beam was used for the repair. As shown, there was no glass substrate damage in the repair area, and the pattern edge shape was repaired neatly. Fig. 7 shows before and after SEM images of a repair done to a minute hole pattern of the same material. A high-quality repair was also achieved in this case. Good optical property evaluation results were obtained for these repair areas at the photomask exposure wavelength[2), 3)].

And, the defect repair performance was evaluated for masks used in extreme ultraviolet (EUV) lithography, a technology that is gaining attention as the next generation in lithography. A 15-keV hydrogen ion (H_2^+) beam was used for the repairs, which verified its practicality[1)].

CONCLUSIONS

FIB technology enabling nanometer-scale imaging, material removal and deposition with a single system has been applied to repairing defects in lithography photomasks, helping make higher integration possible in semiconductor integrated circuits. To support cutting-edge minute patterns of 20 nm or less, Hitachi developed a mask defect repair system with a new GFIS built-in. This system was used to repair defects in photomasks and EUV masks for cutting-edge devices, confirming its practicality.

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Featured Articles

Measurement of Microscopic Three-dimensional Profiles with High Accuracy and Simple Operation

—AFM5500M Scanning Probe Microscope—

Satoshi Hasumura
Shigeru Wakiyama
Masato Iyoki
Kazunori Ando

OVERVIEW: SPMs are able to measure the surface profile of a sample and its mechanical and electrical characteristics with sub-nanometer resolution. Hitachi High-Tech Science developed the AFM5500M SPM, which can accurately measure three-dimensional profiles, to meet demand from industrial measurement applications. Its simple operation reduces the operator's workload by providing features such as an automatic adjustment mechanism for the optical axis of the cantilever and automatic adjustment of measurement parameters. It also has a linkage function for correlation with an SEM or a CSI to enable complementary observation and measurement, and measurement of physical properties of the same area on the sample. This article describes the AFM5500M and its linkage function together with example measurements.

INTRODUCTION

A scanning probe microscope (SPM) is a type of microscope that obtains an image by tracing a needle-sharp tip (probe) over the surface of the object being observed or measured. Fig. 1 shows images obtained by an SPM. An SPM can scan areas with sizes ranging from several hundred microns to several nanometers, and can observe surface profiles with sub-nanometer resolution when scanning small areas. Typically, the resulting images are displayed on a personal computer (PC) monitor, with magnification reaching more than 10 million times when the images are displayed 10-cm square.

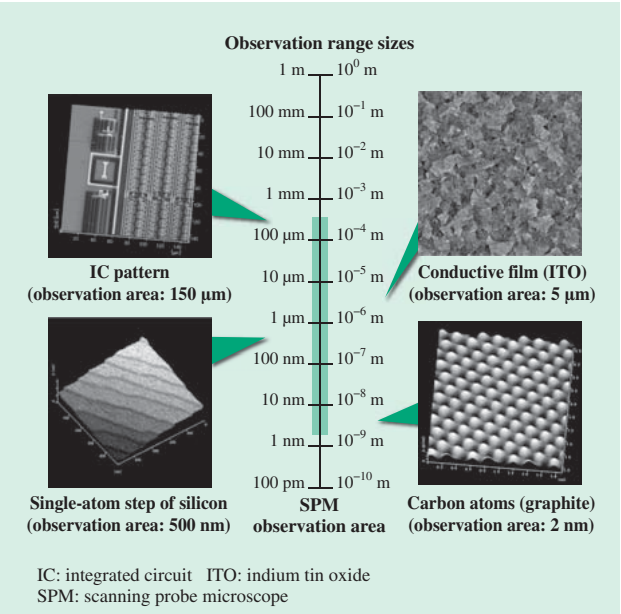


Fig. 1—Example Images Taken by an SPM.
The figure shows the observation range of an SPM and various example images. An SPM has the resolution for atomic imaging.

Other microscopes used for observing surface profiles include scanning electron microscopes (SEMs) and coherence scanning interferometers (CSIs). These other microscopes can obtain images of a large area more quickly than an SPM. However, an SPM has superior resolution, both horizontal and vertical, and can measure length and other physical properties in three-dimensions. This means that the ability to correlatively use these different types of microscopes enables complementary observation and measurement that takes advantage of their respective capabilities.

This article describes the measurement principles and configuration of an SPM, and introduces the AFM5500M SPM released in March of 2016.

SPM MEASUREMENT PRINCIPLES

Principles of Measurement

Fig. 2 shows how SPM measurement works. It uses a needle-sharp tip (probe) on the end of a cantilever.

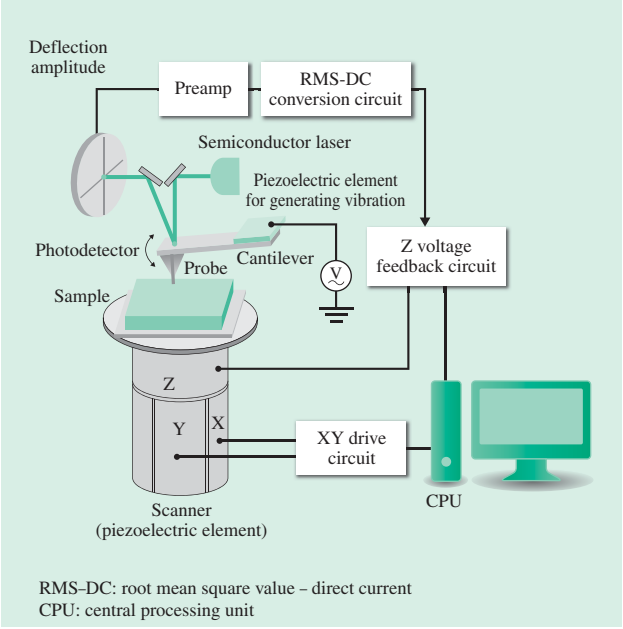


Fig. 2—Principles of SPM Measurement.
The force between the cantilever and the sample causes deformation of the cantilever (deflection amplitude of the lever in the case of a repulsive force). The deformation of the cantilever is detected optically.

When the cantilever is made to vibrate, causing the probe to approach the sample, the resulting physical force between probe and sample causes a change in the cantilever vibration amplitude. This amplitude is detected by shining light on the back of the cantilever.

The sample is place on top of a scanner that is able to move very short distances in the horizontal (X and Y) and vertical (Z) directions. As the scanner scans horizontally with the probe close to the sample, the distance between the probe and the sample varies depending on the surface profile of the sample, causing the cantilever amplitude to vary. This allows the surface profile of the sample to be determined by controlling the vertical position of the scanner so as to keep the cantilever amplitude constant and converting this movement into a three-dimensional image.

Features and Applications

Fig. 3 shows the features and applications of SPMs. Along with high-magnification observation and measurement of three-dimensional profiles, an SPM can also obtain information about the physical properties of the sample surface through techniques such as using a coated cantilever or causing the scanner and cantilever to vibrate. Together with the ability to perform measurements in atmosphere, vacuum, or liquid, the technology is being adopted in a wide variety of fields.

AFM5500M SPM

AFM5500M Precision Probe Microscope

In applications such as electronic components where progress on scaling continues to be made, and for

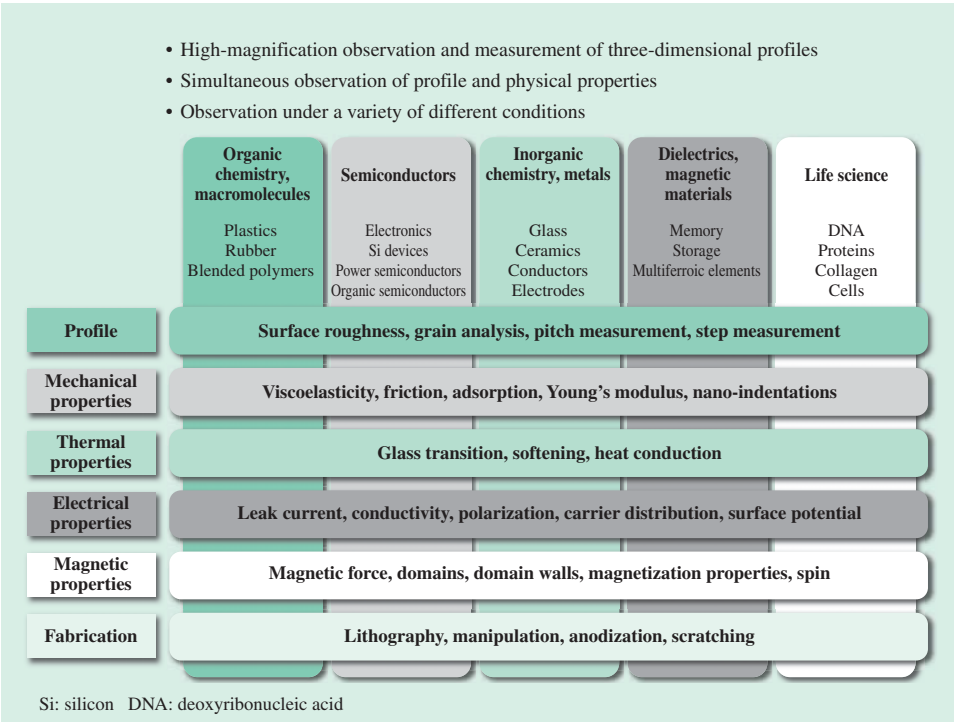


Fig. 3—SPM Features and Applications.
SPMs are used for observation and measurement in a large number of different fields.

Fig. 4—AFM5500M SPM.
Designed as an SPM with a high level of precision and automation, the AFM5500M went on sale in March of 2016.

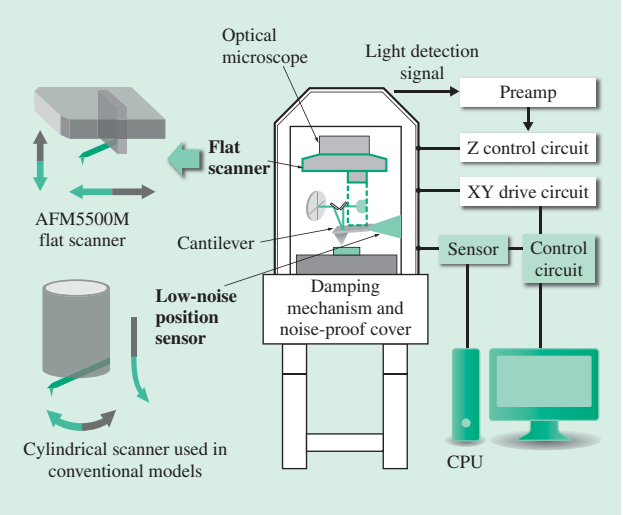


Fig. 5—Configuration of AFM5500M.
A low-noise position sensor and a newly developed flat scanner with high orthogonality and a wide 200-µm range are located near the cantilever.

highly functional materials and precision parts, there is growing demand for SPMs that can measure at even higher resolution for use in development, manufacturing, and quality management. Hitachi High-Tech Science Corporation developed the AFM5500M SPM in response to this demand, designing it for greater precision and automation. Fig. 4 shows a photograph of an AFM5500M and Table 1 lists its main specifications.

Achieving Superior Measurement Precision

To combine high measurement precision and sensitivity with a wide scanning range, the AFM5500M has adopted a technique not used on conventional SPMs. The AFM5500M has a wide-area flat scanner that incorporates a piezoelectric element in the parallel spring mechanism of the cantilever, and Low-noise position sensor for the three axes (horizontal and vertical) located near the cantilever (see Fig. 5). Whereas previous scanners have had problems with arc error and Z-axis orthogonality due to use of a cylindrical piezoelectric element, the AFM5500M is able to obtain distortion-free three-dimensional images by using a flat scanner and reading the vertical sensor while using a sensor to control horizontal scanner movement.

Fig. 6 shows a measurement by the AFM5500M of a step in an amorphous silicon film on a silicon substrate. Whereas conventional scanners introduced arc error into measurement data, the AFM5500M is capable of performing measurements with good uniformity over a wide 200-µm range.

Fig. 7 shows a measurement by the AFM5500M of the texture of a photovoltaic cell. The poor Z-axis orthogonality of conventional scanners results in asymmetrical measurement of the left and right angles. The AFM5500M, however, is able to accurately

TABLE 1. AFM5500M Main Specifications
The wide-area flat scanner is on the cantilever side and the automatic XY stage is on the sample side. The AFM5500M features a wide scanning range, measurement precision, and ease of use (automation).

Parameter	Value
Scanner range (observation range)	XY: 200 µm Z: 15 µm
Nonlinearity	<0.2% (X,Y,Z)
XY orthogonality	<0.5°
Bow	2 nm (50-µm area)
Maximum sample size	ϕ: 100 mm, thickness: 20 mm

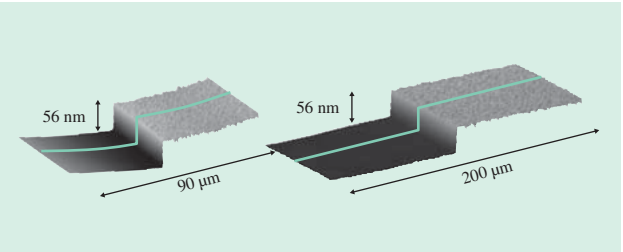


Fig. 6—Step Measurement of Amorphous Silicon Thin Film.
A measurement performed using a conventional model is shown on the left and the AFM5500M measurement is on the right. This demonstrates the uniformity of measurement over a wide area.

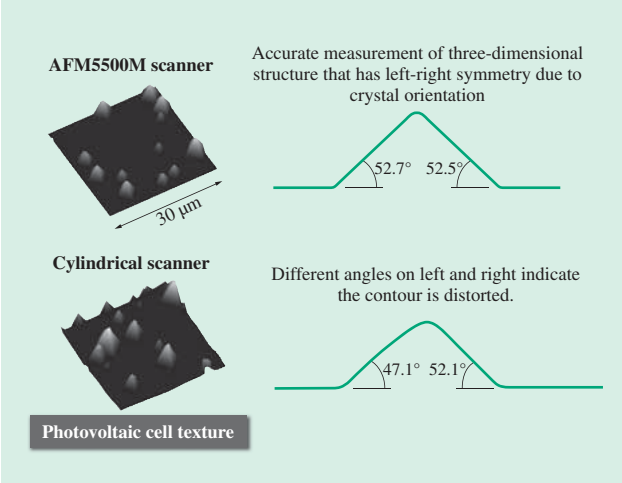


Fig. 7—Measurement of Photovoltaic Cell Texture.
The AFM5500M measurement is shown on the top and the measurement performed using a conventional model is on the bottom. This demonstrates the underlying superior performance of the AFM5500M in terms of things like Z-axis orthogonality and horizontal nonlinearity.

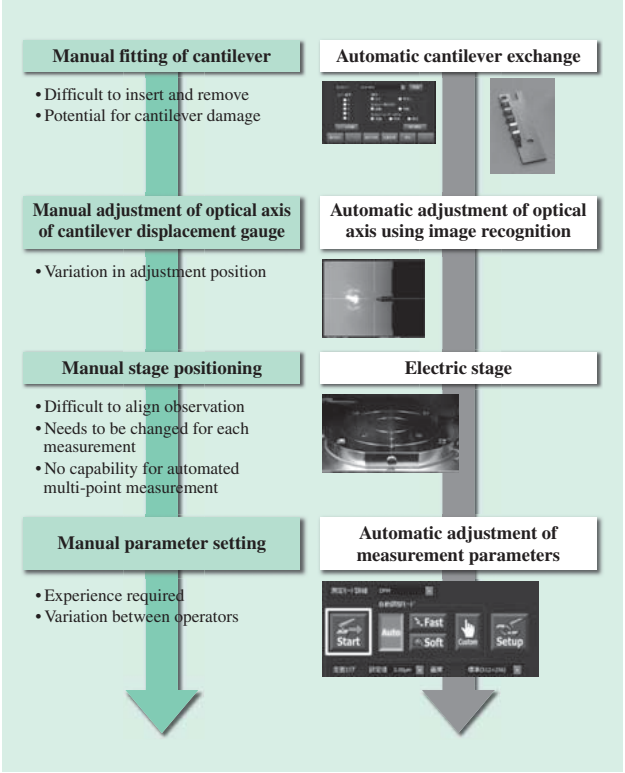


Fig. 8—SPM Measurement Procedure.
The conventional measurement procedure is shown on the left and the procedure for the AFM5500M is on the right. Automation has significantly simplified the procedure.

measure this three-dimensional structure, which has left-right symmetry due to the crystal orientation. This demonstrates how the AFM5500M is capable of highly precise profile measurement, without the profile distortion and asymmetry that have been problems for SPM measurement.

Improved Operation through Measurement Automation

Fig. 8 shows a flowchart of the operator's procedure when making an observation or measurement. The AFM5500M uses pattern matching and other techniques to automate the insertion of the cantilever and adjustment of the optical axis, and is equipped with functions for automatically adjusting the cantilever amplitude and feedback parameters. These functions make it easy for the operator to perform observation and measurement without the need for complicated procedures, they also eliminate measurement errors due to the operator.

TRIAL CORRELATION BETWEEN OBSERVATION EQUIPMENT

As noted in the introduction, the ability to correlatively use different types of microscopes enables complementary observation and measurement that takes advantage of their respective capabilities. To achieve this, Hitachi High-Tech Science has developed quick and simple observation techniques that use a

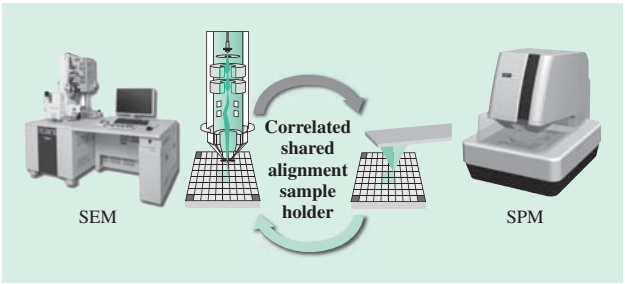
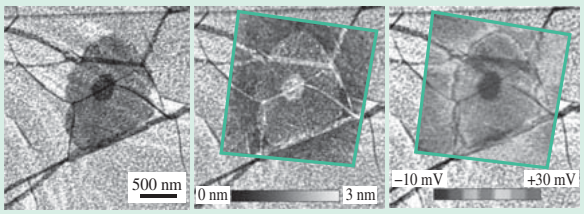


Fig. 9—Concept of Correlation between Instruments.
By using a shared alignment sample holder and sharing the alignment marks and measurement coordinates, it is possible for different instruments to observe the same area of the sample.

number of different microscopes to image the same location by using a shared alignment sample holder and a coordinate linkage function (see Fig. 9).

Fig. 10 shows images acquired from the same location on monophase graphene/silicon dioxide (SiO_2) grown by chemical vapor deposition (CVD) using both an SEM and an SPM. To investigate the cause of contrasts present in the SEM image, the image was overlaid with SPM images of topography and surface potential. This showed that the difference in contrasts on the SEM image correspond to the height



SiO_2: silicon dioxide CVD: chemical vapor deposition

Fig. 10—Monophase Graphene/SiO_2 grown by CVD. The initial SEM image is shown on the left, overlaid with the SPM topography in the center, and overlaid with the SPM surface potential image on the right.

of one layer of graphene observed by the SPM, and that the surface potential varies with factors such as the number of layers of graphene[(1)].

CONCLUSIONS

This article has described the principles and features of an SPM. It has also described the AFM5500M, an SPM suitable for applications ranging from nano-scale research and development to industrial measurement and quality management.

Along with a high level of measurement precision thanks to features that include a newly developed scanner and low-noise sensors, this latest SPM also features significant improvements in ease-of-use, including automation of cantilever exchange and optical axis adjustment. And, as a new trial, the article also presents an example of its use in observing and measuring the same location with a number of different microscopes.

In anticipation of the growth in demand for nano-scale measurement in industry, Hitachi High-Tech Science intends to continue developing the instrument with the aim of improving precision, speed, and resolution. Hitachi High-Tech Science also intends to supply customers with total solutions that correlate a number of different microscopes together to make it easy to perform the steps from observation to analysis and measurement.

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Featured Articles

Measurement of Surface Profile and Layer Cross-section with Wide Field of View and High Precision

—VS1000 Series Coherence Scanning Interferometer—

Yugo Onoda, Ph.D.
Kiyotaka Ishibashi
Kaori Yanagawa
Yoshihiro Sato

OVERVIEW: Techniques for measuring thin films and surfaces have become an essential part of the technology underpinning our way of life in recent years. Examples include a wide variety of thin films now in use, such as the advanced films used in smartphones or the electrolyte membranes used in fuel cells, and controlling the surface roughness of pistons used in engines to improve their fuel economy. Hitachi High-Tech Science has released the VS1000 series CSI, extending its range of models that provide solutions for these types of surface analysis. CSI can be used to perform three-dimensional measurement of surface profiles, surface roughness, and film thickness. Measurements can be performed in just a few seconds and provide high vertical resolution (0.01 nm) over a wide measurement range (several millimeters). Another feature is that they can perform non-contact and non-destructive measurement of thickness and cross-sections of multi-layer transparent film, and detect the presence of contaminants in the film, peeling, or other defects.*

INTRODUCTION

COHERENCE scanning interferometer (CSI) uses optical interference to measure surface profiles. Fig. 1 shows how CSI compares to other forms of three-dimensional profile measurement. CSI takes a few seconds to measure a wide area (up to 7.1 mm × 5.3 mm) with similar vertical resolution to a scanning probe microscope (SPM) (0.01 nm). This makes CSI suitable for obtaining surface profiles for an entire specimen with high height precision. Furthermore, being a non-contact method of measurement that uses light means that it does not damage or contaminate the specimen. Another feature is its ability to measure the thickness of multi-layer transparent film.

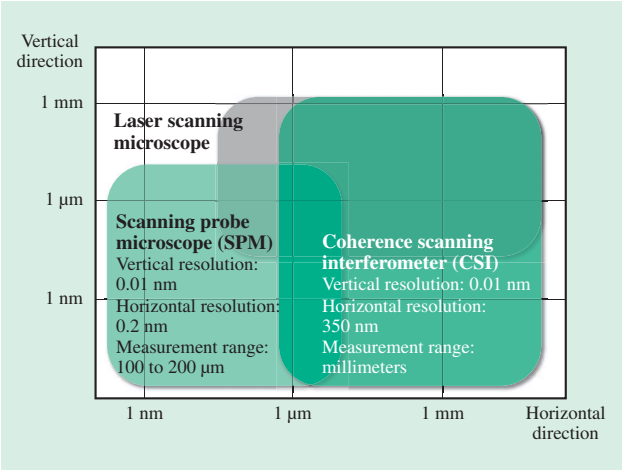

Fig. 1—Role of CSI in Three-dimensional Profile Measurement Instruments.
CSI is a solution for surface analysis that is complementary to an SPM.

CSI MEASUREMENT PRINCIPLES AND OPTICS

Fig. 2 shows the optics of a CSI microscope. White light from the light source first passes through a band pass filter to eliminate all but a particular wavelength of light. The light then enters the two-beam interference objective lens where the beam splitter splits it into two components, one to the reference mirror and one to the specimen. The light reflected back from the reference mirror and specimen respectively is then captured by

* VS1000 series is only sold in Japan.

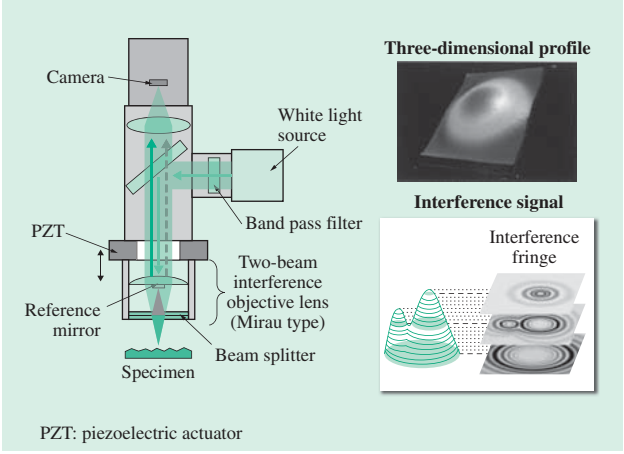

Fig. 2—CSI Optics and Interference Fringe Image.
An interference signal is obtained by using a piezoelectric actuator to vary the distance between the beam splitter and the specimen surface. This interference signal is then converted into a three-dimensional profile.

the camera. An interference signal of bright and dark fringes is formed by using a piezoelectric actuator to move the objective lens in the Z direction, thereby varying the distance between the beam splitter and the specimen. The surface profile of the specimen is then determined by using a proprietary algorithm to convert this interference signal into height information[(1)].

Whereas the vertical resolution of a conventional optical microscope varies due to the changing of the focal depth in accordance with the magnification of the objective lens, because CSI uses optical interference, the vertical resolution remains constant regardless of the objective lens magnification. As a result, it can achieve a high vertical resolution of 0.01 nm across the full range from low magnification/wide field of view to high magnification/narrow field of view.

TABLE 1. VS1550 Main Specifications
CSI can achieve a high level of vertical resolution over a wide area. It is also possible to produce images of regions up to tens of millimeters in size by using a function for stitching images together.

Parameter	Value
Specimens	Height: 90 mm or less Weight: 1 kg or less
Automatic XY stage	Movement: XY ± 75 mm
	Specimen surface: Width 160 mm × Depth 160 mm
Vertical resolution	0.01 nm (max.)
Horizontal resolution	340 nm (for × 110 objective lens)
Maximum measurement area	7.1 mm × 5.3 mm (single field of view)

VS1000 SERIES CSI

The VS1000 series CSI is available in four models to suit different specimen sizes: the VS1330, VS1530, VS1540, and VS1550. Table 1 lists the main specimen specifications of the top-end model, VS1550, and Fig. 3 shows a photograph of it. The VS1000 series can be used to perform measurements on larger specimens compared to scanning electron microscopes (SEMs) and SPMs.

EXAMPLES OF SURFACE PROFILE MEASUREMENT USING CSI

Quantitative Height Measurement Using CSI

Fig. 4 shows an image obtained using CSI and a backscattered electron image from an SEM. The image obtained by CSI matches that obtained by the SEM, and the cross-section profile measurement data indicates a grain height of 16 µm. The SEM is able to perform accurate topographical observations with high horizontal resolution and the CSI can obtain quantitative height measurements, enabling grain size to be determined with high precision from multiple perspectives.

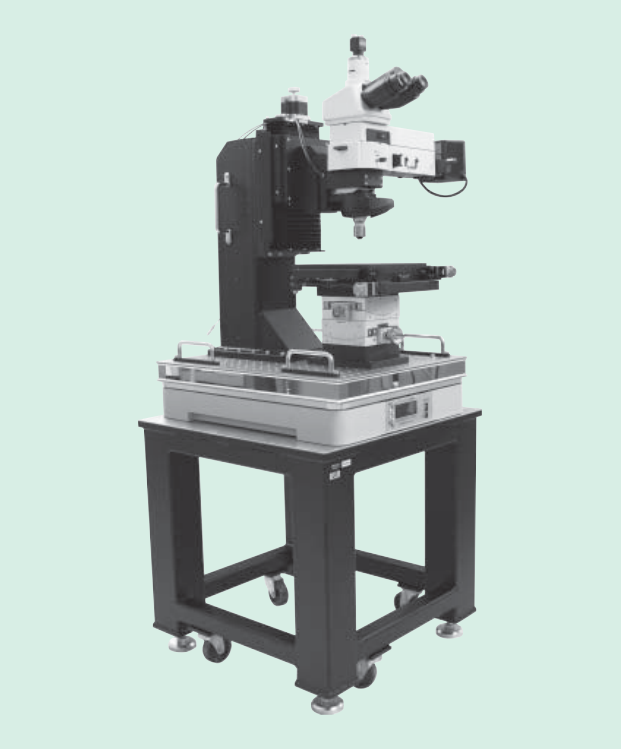

Fig. 3—VS1550 CSI.
The VS1550 is the top-end model in the VS1000 series.

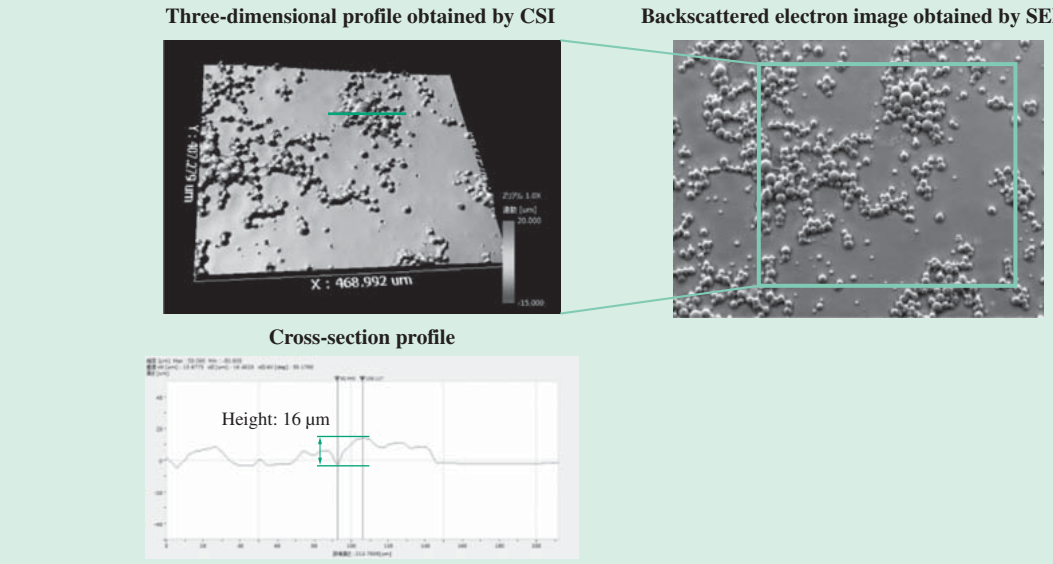

Fig. 4—Comparison of CSI and SEM Images.
Observations were made of the same area on a food package that had been made water repellant. A feature of the image obtained by CSI is that it matches that obtained by the SEM and also provides quantitative height data.

Profile Measurement with High Aspect Ratio

Fig. 5 shows an example measurement of a groove with a high aspect ratio (narrow and deep). The profile can be measured all the way to the bottom of the groove despite having an aspect ratio of 14 (4 µm wide and 57 µm deep). Profiles with a high aspect ratio have been a problem for other types of microscopes, with the light of the laser scanning microscope or the cantilever of the SPM having difficulty reaching the bottom of the groove. Taking advantage of the fact that the vertical resolution with CSI is not dependent on the magnification of the objective lens, it can measure profiles with a high aspect ratio by using an objective lens with low magnification and keeping the numerical aperture (NA) low so that the light reaches the bottom without being focused.

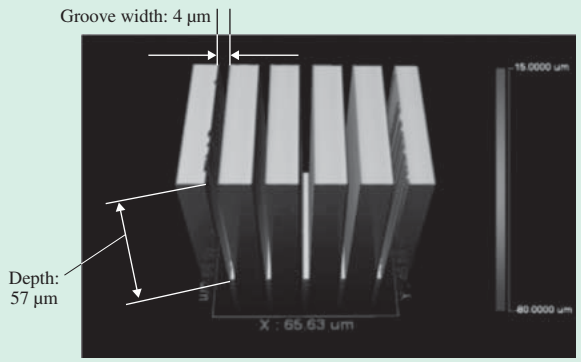

Fig. 5—Measurement of Deep Groove.
By taking advantage of the high level of vertical resolution, measurement of a groove with a high aspect ratio is possible even with a low-magnification lens.

Use of Wide-angle Measurements to Identify Linear Defects and Irregularities

Fig. 6 shows a profile measurement of the surface of wrapping film. While there is visible evidence of linear defects, measurements taken over a small area are unable to identify the difference between areas where the defect is and is not present. The use of CSI to perform a wide-angle measurement (on the order of millimeters) over the entire specimen indicates that the surface profile is different in areas where the defect is present, and it can be used to measure the localized differences in roughness between areas with and without the defect. This is an example of the benefits of being able to combine a high level of vertical resolution with low magnification and a wide field of view.

Use in Tribological Measurement

Automotive piston heads are engraved with grooves several micrometers in size that enable the lubricant to spread more easily. Fig. 7 shows a surface representing

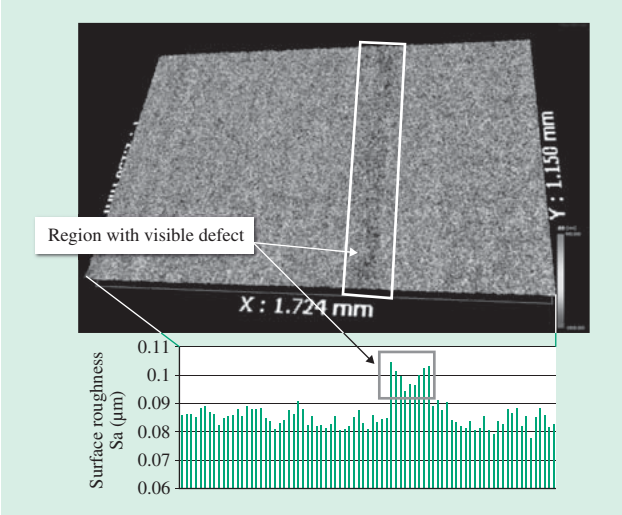

Fig. 6—Linear Defects in Wrapping Film.
The differences in surface profile and roughness between areas with and without the defect can be identified by wide-angle measurement

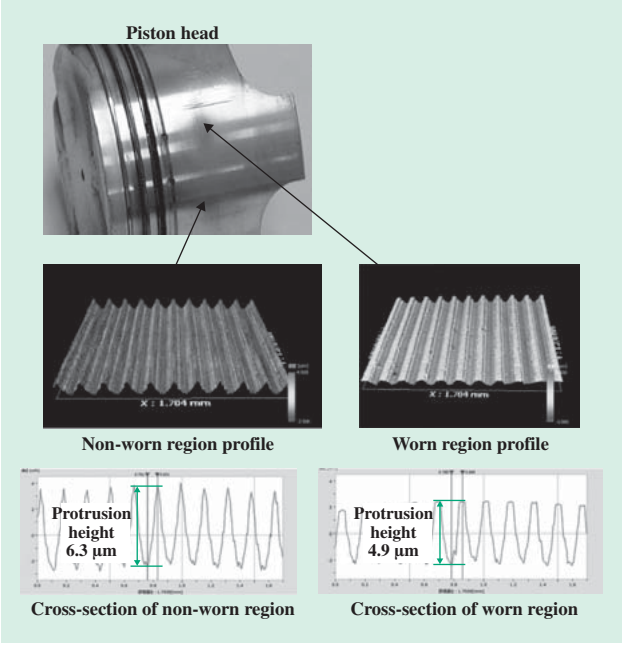

Fig. 7—Comparison of Worn and Non-worn Regions of Piston Head.
CSI provides height information and can quantitatively determine the condition of protrusions in worn and non-worn regions.

the variation in wear. Measurement of a worn region shows that the protrusions have been worn down by 1.4 µm. As the VS1000 series can determine surface quality (roughness measurement) in accordance with the International Organization for Standardization (ISO) 25178 international standard for surface roughness, it can quantitatively assess the degree of wear.

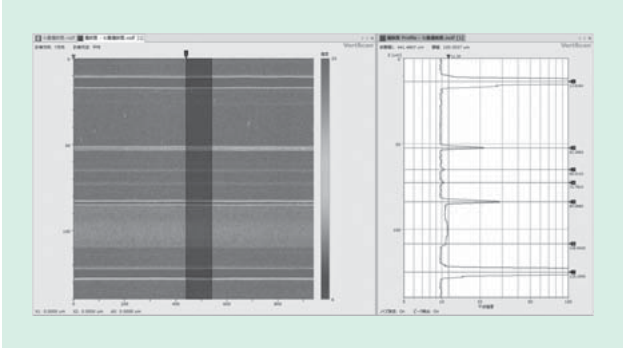

Fig. 8—Cross-section Analysis of Six-layer Wrapping Film.
The VS1000 series can measure the thickness of multi-layer transparent film using a proprietary detection method.

MEASUREMENT OF FILM THICKNESS BY ANALYZING FILM CROSS-SECTION

CSI can be used to measure the thickness of multi-layer transparent film and detect the presence of contaminants, peeling, or other defects. By using the interference signal obtained from the optical boundaries within multi-layer film to generate images of the multi-layered structure, this provides a non-destructive technique for determining the layer structure of multi-layer film or its internal condition without making a cross-section. Fig. 8 shows an analysis of the cross-section of a six-layer film used for wrapping. It indicates how the interference due to each boundary can be interpreted as a cross-section image. It also obtains depth information on any defects such as air bubbles present in the film layers. Measurement of the internal film thicknesses is possible because thicknesses with an optical distance of 1 µm or more can be resolved in the interference signal. This measurement can be performed even if the difference between the refractive indices of the optical boundaries is small. Because the measurement is performed from the top surface, another feature is that, if the top surface profile is flat, it will be seen as being flat even if the substrate is uneven.

CONCLUSIONS

This article has described how, by using optical interference, CSI can perform non-contact and non-destructive measurements over a wide area, quickly, and with high vertical resolution.

By adding the VS1000 series CSI to its range of surface analysis solutions alongside SEMs and SPMs, Hitachi High-Tech Science Corporation intends to provide advanced solutions that contribute to the latest leading-edge business development by customers.

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Featured Articles

Fluorescence Pattern Analysis to Assist Food Safety

—Food Analysis Technology Driven by Fluorescence Fingerprints—

Jun Horigome
Michinari Kozuma
Toshihiro Shirasaki, Ph.D.

OVERVIEW: Fluorescence fingerprint analysis uses the large quantity of information contained in fluorescence patterns generated by organic components in samples to identify quality or place of origin, or to detect harmful substances. It is a simple and low-cost method that is gaining attention for its food industry applications. The Fluorescence Spectrophotometer F-7100 made by Hitachi High-Tech Science incorporates several technologies that enable high-throughput fluorescence fingerprint measurement. It is designed to have a full range of specialized functions for fluorescence fingerprint measurement, such as a new automatic filter accessory device that simply and rapidly removes the effect of spectrometer-specific higher-order light. This article presents its features and some example applications.

INTRODUCTION

FLUORESCENCE fingerprint analysis measures the fluorescence pattern (fluorescence fingerprint) emitted by a sample and performs statistical multivariate analysis on a massive quantity of numerical data representing parameters such as fluorescence wavelength and intensity. Recent advances in information processing technology have enabled analysis of large-volume data, making fluorescence fingerprint analysis practical and expanding its scope of application. The level of attention being paid to food industry applications has increased dramatically over the past few years, with expectations for applications such as the identification of sample types and places of origin[(1), (2)], the calculation of sample mixture ratios[(3)], the detection of harmful substances such as mycotoxins[(4) - (7)], and the quantification of functional components.

This article describes the fluorescence fingerprint analysis method and its features, and presents some of the latest example applications.

FLUORESCENCE FINGERPRINT ANALYSIS

Fluorescence Fingerprints

When light (excitation light) is shone on a sample, light of various wavelengths (fluorescent light) is emitted from the organic substances contained in the sample. Fluorescent light contains three items of information: the wavelength of the excitation light (the excitation wavelength), the wavelength of the fluorescent light from the sample (the fluorescence wavelength), and the intensity of the fluorescent light from the sample (the fluorescence intensity). A fluorescence fingerprint is obtained by plotting these items of information in three dimensions as an aerial view or contour map.

As an example, Fig. 1 shows the fluorescence fingerprint of a sample of pineapple juice. The excitation wavelength is shown on the vertical axis, the fluorescence wavelength is shown on the horizontal axis, and the fluorescence intensity is represented by contour lines. The plot resembles a human fingerprint, and is therefore called a fluorescence fingerprint. Since fluorescent light is observed at longer wavelengths than excitation wavelengths (Stokes' law), the fluorescence fingerprint appears at the bottom-right of the diagonal. The fluorescence intensity is plotted in the form of contour lines since changing the excitation wavelength will not result in a change in fluorescence wavelength for the same component.

Peaks (a) to (e) were detected in this fluorescence fingerprint. These peaks come from the fluorescent components contained in the sample. From previously reported examples[(8)], it can be inferred that they include (a) L-tyrosine from aromatic amino acid, (b) L-tryptophan, (c) ferulic acid and lignins from cell walls, (d) vitamin B_2 (riboflavin), and (e) chlorophylls. Different places of origin or growth conditions will cause changes in the quantities of these components,

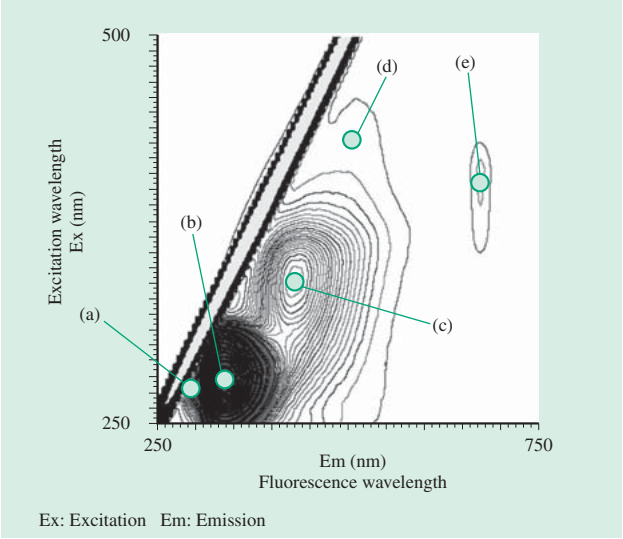

Fig. 1—Fluorescence Fingerprint Example (Pineapple Juice). The vertical axis represents the excitation wavelength, the horizontal axis represents the fluorescence wavelength, and the contour lines represent the fluorescence intensity. Peaks were detected for fluorescent components (a) to (e) contained in the sample. From previously reported examples, it can be inferred that they include (a) L-tyrosine from aromatic amino acid, (b) L-tryptophan, (c) ferulic acid and lignins from cell walls, (d) vitamin B_2 (riboflavin), and (e) chlorophylls.

enabling sample-specific fluorescence fingerprints to be acquired that enable identification of information such as place of origin.

Fluorescence Fingerprint Analysis Method and Identification Applications

Fluorescence fingerprints are a measurement method that has been known for about 30 years. But with a single measurement requiring anywhere from tens of minutes to hours to complete, it was initially an inconvenient method, and required time for data analysis. As a result, only a single wavelength of an excitation light/fluorescent light peak for a component of interest was previously used to identify or quantify the component. Recent improvements in measuring equipment performance and advances in large-volume data analysis technology have enabled the use of statistical methods for comprehensive analysis of fluorescent light and excitation light spectra (large-volume data consisting of information for many wavelengths and intensities), greatly expanding the potential for identification applications.

Fig. 2 is a conceptual diagram illustrating the fluorescence fingerprint analysis method. Multiple samples with characteristics (such as place of origin or quality) that are known beforehand are obtained (these samples are called known samples). The fluorescence fingerprint data of each sample is measured. This data is subjected to multivariate analysis to create an 'identification model' from the known samples. The plotted points in the identification model correspond to each known sample. The fluorescence fingerprint data of the unknown sample is then measured and plotted in the identification model to determine which known sample the unknown sample most closely resembles, enabling identification of its place of origin and quality.

Fluorescence fingerprint data is an aggregate of anywhere from thousands to tens of thousands of data points. To enable use of this large volume of data, multivariate analysis is applied to condense it into a small number of variables that express the data's features. For example, principal component analysis is a method that lowers the dimensions of large-volume data by condensing it into variables (feature values) called principal component scores. By using principal component scores 1 and 2 on the horizontal and vertical axes, the identification model of Fig. 2 displays large-volume fluorescence fingerprint data at a single coordinate using two principal component scores. This plot indicates which group the unknown sample belongs to, enabling easy identification.

Features of Fluorescence Fingerprint Analysis

Fluorescence fingerprint analysis has the following three major features:

(1) Ability to perform identification analysis from a massive quantity of information

The wavelengths of excitation light and fluorescent light are generally measured in a range extending from ultraviolet to visible light (about 200 to 800 nm). The intensity information acquired consists of tens of thousands of data points. This massive quantity of numerical data is subjected to multivariate analysis to condense it into several variables for use in identification analysis.

(2) Simplicity of analysis

Equipment-based analysis of food or farm products generally requires preprocessing involving several procedures. However, fluorescence fingerprint analysis measures the fluorescence possessed by the sample itself (auto-fluorescence), enabling measurement with a minimal amount of preprocessing (such as pulverization, dissolving, or filtration), and direct analysis of samples such as fruit fragments or raw meat. Analysis is also possible on samples in either a liquid or solid state (such as in bar or powder form).

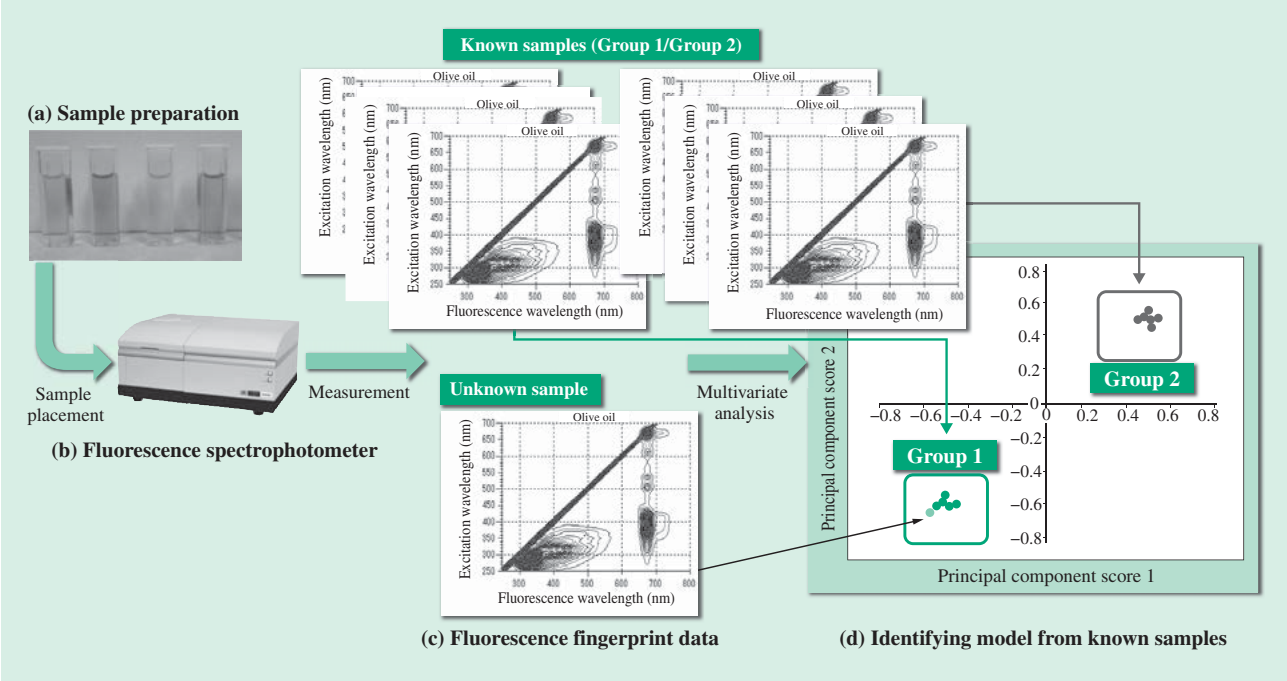

Fig. 2—Concept of Fluorescence Fingerprint Analysis Method.
This method obtains multiple samples with characteristics that are known beforehand (known samples) and measures the fluorescence fingerprint data of each one. This data is subjected to multivariate analysis to create an identifying model from the known samples. The fluorescence fingerprint data of the unknown sample is then measured and subjected to multivariate analysis. The result is plotted over the identifying model, enabling the group that the unknown sample most closely resembles to be inferred.

(3) Lower analysis cost

Fluorescence fingerprint analysis has lower startup and running costs than other methods using analysis equipment. In relation to mycotoxin analysis for example, Fujita et al.[(4) - (7)] reported that fluorescence fingerprint analysis can be expected to lower the cost of analysis when used for sample selection (screening analysis), a preprocess for procedures such as high-cost mass analysis.

FLUORESCENCE FINGERPRINT MEASUREMENT SYSTEMS

Fluorescence fingerprint analysis previously had limited applications due to the time required for measurement. However, advances in the sensitivity and speed of the fluorescence spectrophotometers used for fluorescence measurement that began about ten years ago have improved throughput to the point where a single measurement can be completed in a matter of minutes, enabling a large quantity of fluorescence fingerprint measurements. Fluorescence fingerprint measurement requires scanning of the excitation light from the ultraviolet range to the visible range, and continuous measurement of the wavelength and intensity of the fluorescent light (fluorescent spectrum). Fluorescence spectrophotometers therefore require high-speed/high-precision measurement performance.

Hitachi High-Tech Science Corporation's Fluorescence Spectrophotometer F-7100 has a three-dimensional fluorescent spectrum measurement mode for fluorescence fingerprint measurement. It also incorporates several technologies designed to increase the throughput of fluorescence fingerprint measurement, such as one of the fastest scan speeds in its class (60,000 nm per minute), automatic setting of response processes for high-speed scanning, and rapid excitation wavelength switching (see Fig. 3).

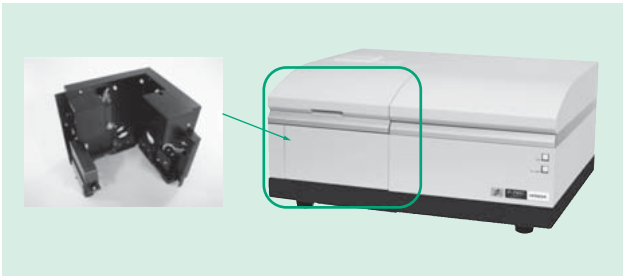

Fig. 3—Appearance of the F-7100 and Automatic Filter Accessory.
Mounting the automatic filter accessory device in the F-7100 enables simple and rapid removal of the effects of higher-order light that appear as ghost peaks.

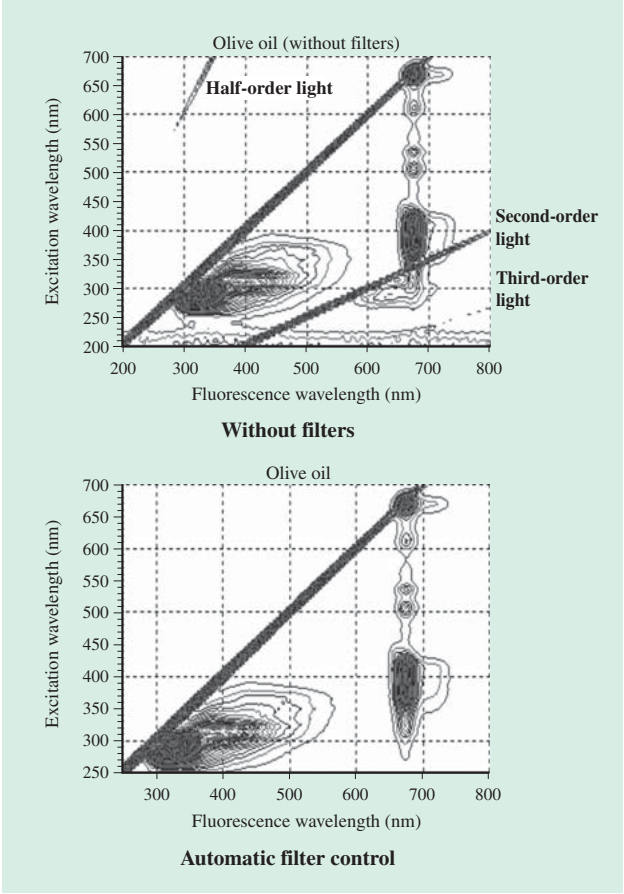

Fig. 4—Comparison of Fluorescence Fingerprint Data With and Without Filters.
The graphs show fluorescence fingerprints for olive oil. Without filters, unneeded spectrometer-specific higher-order light (such as second- and third-order light) is superimposed on the fluorescence fingerprint. The automatic filter accessory automatically inserts a filter corresponding to the measurement conditions, enabling the effects of higher-order light to be eliminated.

One of the challenges of fluorescence fingerprint measurement is removing the effects of spectrometer-specific higher-order light (such as second- or third-order light) that appears as ghost peaks. A new automatic filter accessory was developed to solve this problem. It automatically inserts filters corresponding to the measurement conditions, enabling simple and rapid removal of the effects of higher-order light (see Fig. 4). To improve data analysis precision, the number of effective data points that can be used in fluorescence fingerprint analysis has been increased from about 4,500 to about 10,000 for the standard wavelength range. The data processing unit has also been given a full range of specialized functions for fluorescence fingerprint measurement, such as a fluorescence fingerprint peak display function, and a function for transferring data to multivariate analysis software.

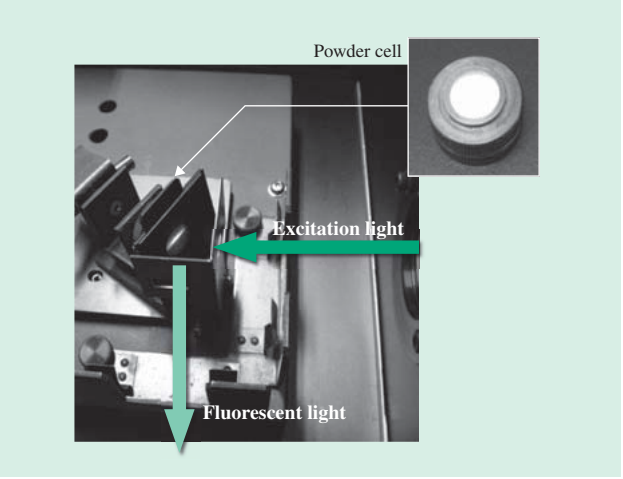

Fig. 5—Sample Placement.
To measure the fluorescence fingerprint of starch, about 0.7 mL of the sample was sealed in a powder cell, which was placed in a solid sample holder enabling measurement of the fluorescent light from the sample's surface.

EXAMPLE APPLICATIONS

Identifying Starches by Their Raw Materials

Using samples of starch from corn, potatoes, and wheat, Hitachi High-Tech Science attempted to identify each type of starch from the results of measuring its fluorescence fingerprint. About 0.7 mL of each sample was sealed in a powder cell, which was placed in a solid sample holder enabling measurement of the fluorescent light from the sample's surface (see Fig. 5). Fig. 6 shows the fluorescence fingerprints obtained. Hitachi High-Tech Science found several peaks for each sample. The peaks observed near the 300-nm fluorescence wavelength are hypothesized to come from amino acid components of proteins. The aerial views of the fluorescence fingerprints make it difficult to identify the differences in the samples. However, while the samples had no major differences in peak wavelengths, differences were found in their peak intensities. Hitachi High-Tech Science therefore extracted the fluorescence intensity of typical wavelengths corresponding to intensity peaks and valleys, and performed multivariate analysis (principal component analysis).

Fig. 7 shows the results. As the figure shows, the plot for each raw material is grouped differently. Furthermore, the mixed sample has a different plot position from the pure samples and is hypothesized to be a mixture made from corn and potato starches. So, by applying principal component analysis to fluorescence fingerprint data as described, it should be possible to identify what raw material an unknown

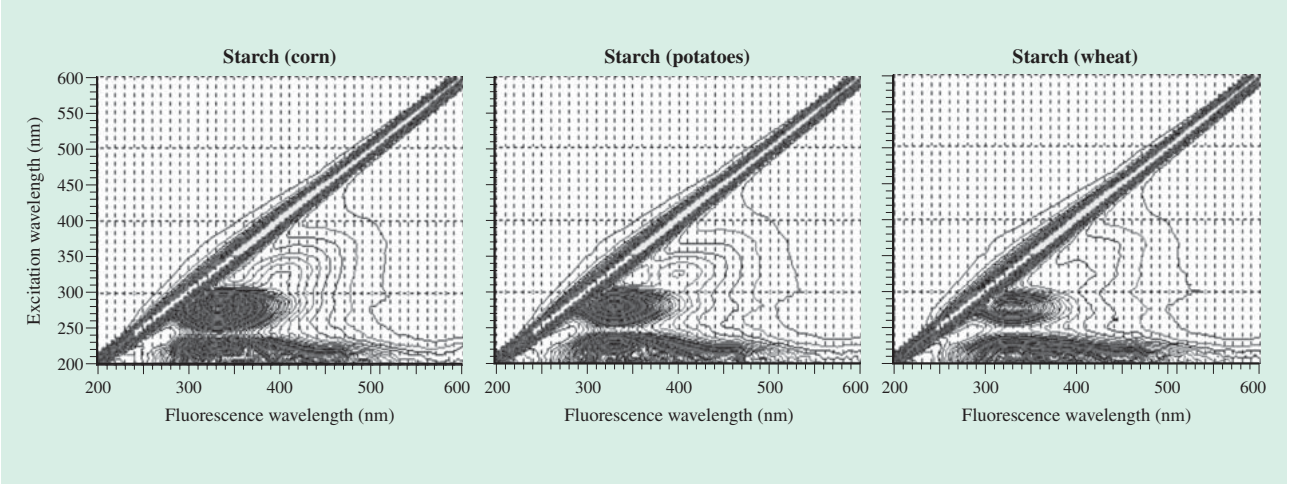

Fig. 6—Fluorescence Fingerprints of Starch from Different Raw Materials.
The graphs show the fluorescence fingerprint of starch from corn (left), potatoes (middle), and wheat (right). The peaks observed near the 300-nm fluorescence wavelength are hypothesized to come from amino acid components of proteins. No major differences were found in the peak wavelengths that appeared for each sample, making it difficult to identify differences in the fluorescence fingerprints from the aerial views.

sample is made from, for applications in quality control and defective product analysis.

Analysis Identifying Olive Oil

Hitachi High-Tech Science measured the fluorescence fingerprint of samples of commercially available, regular olive oil and virgin olive oil. Fig. 8 shows the measurement results. The samples were placed in cells made of polymethyl methacrylate (PMMA) without dilution or other preprocessing, and the fluorescent light from the surfaces of the samples was measured. For all of the olive oil samples, Hitachi High-Tech Science found fluorescence peaks in two regions: Region 1 (with an excitation wavelength of 250 to 450 nm and fluorescence wavelength of 300 to 600 nm), and Region 2 (with an excitation wavelength of 300 to 700 nm and fluorescence wavelength of 650 to 750 nm). Region 1 suggests fluorescence corresponding to an oxidation product, and Region 2 suggests fluorescence corresponding to chlorophyll[8]. The fluorescence intensity of fluorescence peak (i) (excitation wavelength of 320 nm, fluorescence wavelength of 400 nm) was extracted from Region 1, and the fluorescence intensity of fluorescence peak (ii) (excitation wavelength of 415 nm, fluorescence wavelength of 675 nm) was extracted from Region 2. Hitachi High-Tech Science calculated the fluorescence intensity ratio [(ii)/(i)]. As shown by the numbers in the graphs in Fig. 8, a comparison of fluorescence intensity ratios indicates that the values are higher for virgin olive oil than for regular olive oil.

Virgin olive oil is extracted from the olive fruit and is not refined or processed, which results in a high level of the chlorophyll contained in the olive fruit being detected [fluorescence peak (ii)]. On the other hand, the chlorophyll content of regular olive oil may be reduced through refining and processing,

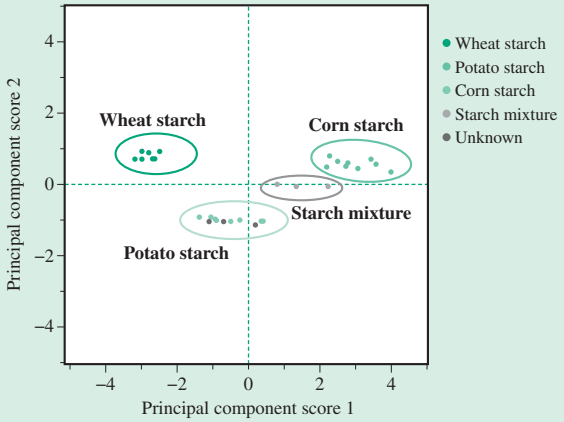

Fig. 7—Principal Component Analysis Results for Starch Fluorescence Fingerprints.
Principal component analysis lowers the dimensions of large-volume data by condensing it into principal component scores, which are variables that represent data features. The plot for each raw material falls into a distinct grouping, making it easy to identify the differences among the samples. The mixed sample is hypothesized to be a mixture of corn starch and potato starch. The unknown sample is hypothesized to be potato starch.

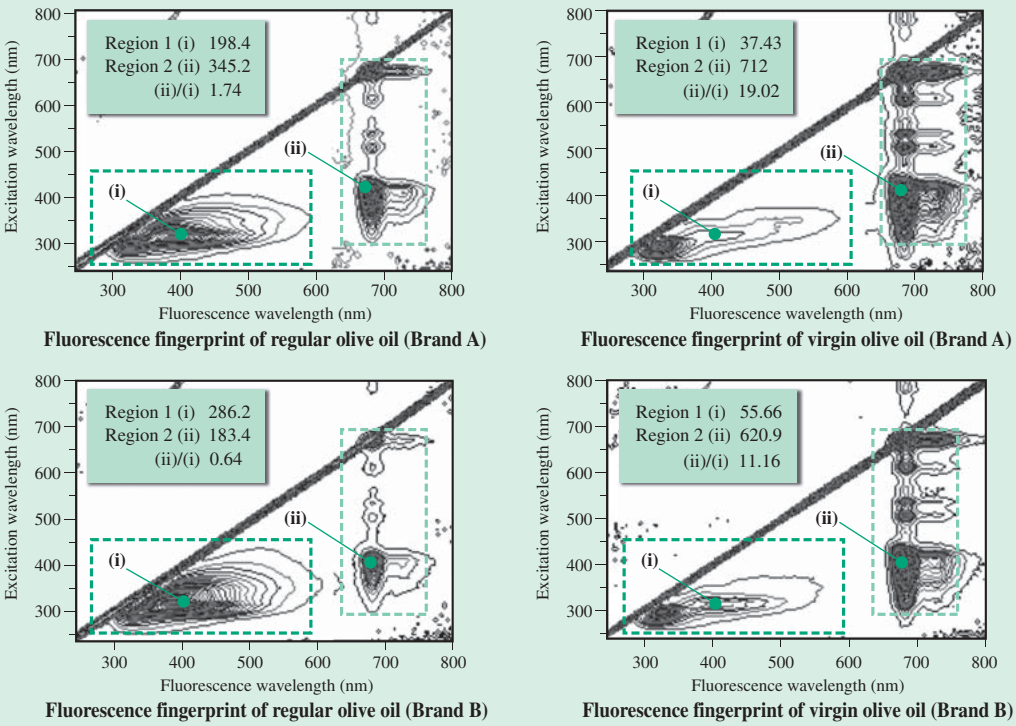

Fig. 8—Olive Oil Fluorescence Fingerprints.
Fluorescence peaks were found in two regions: Region 1 (excitation wavelength of 250 to 450 nm, fluorescence wavelength of 300 to 600 nm), and Region 2 (excitation wavelength of 300 to 700 nm, fluorescence wavelength of 650 to 750 nm). The fluorescence intensity ratio [(ii)/(i)] was calculated to identify the differences between regular and virgin olive oils.

which results in a low level of chlorophyll being detected. Similarly, the fluorescence corresponding to an oxidation product [fluorescence peak (i)] is lower in virgin olive oil. In practice, the quality of olive oil is determined by criteria such as its acidity, aroma, and flavor. So, while this method cannot determine olive oil quality, fluorescence fingerprint data can be used to enable simple evaluation of counterfeit vegetable oil products, a topic that has been in the spotlight recently.

CONCLUSIONS

A wide variety of samples exist in the food industry, with assessment criteria that also vary greatly according to the objective. Research has therefore been done on expanding applications, such as creating analytical methods that are tailored to samples and objectives[6]. Many sources have reported research results about attempts to apply fluorescence fingerprint analysis to the food industry, and awareness of the method has been increasing dramatically over the past few years. Fluorescence fingerprint analysis was created as a measurement method that is simpler and faster than conventional methods. Hitachi High-Tech Science will continue working on developing applications and improving equipment function/performance to help this technology contribute to society.

ACKNOWLEDGMENTS

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Featured Articles

Compact Mass Detector for Drug Discovery Research

—Chromaster 5610 Mass Detector—

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Norimasa Minamoto
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Kosaku Toyosaki
Shinji Yoshioka

OVERVIEW: Mass spectrometers are widely used in a variety of different scientific fields, including synthetic organic chemistry and biochemistry. Hitachi High-Tech Science commercialized the Chromaster 5610 MS Detector, a mass detector that is easy for a wide range of users to use, and is based on a new concept that is different from that of large mass spectrometers. This article describes examples of how this analyzer is used in the field of drug discovery research.

INTRODUCTION

MASS spectrometry (MS) is a technique for measuring the masses of the constituent molecules of a sample by ionizing them in the presence of a high voltage. It is widely used in a variety of different scientific fields, including synthetic organic chemistry and biochemistry, with the mass information being used to identify sample constituents, analyze their structure, and quantify them.

In the pharmaceutical sector in particular, mass spectrometry is used in all stages from drug discovery research to clinical testing and production management. While this mainly involves structural analysis using a high-resolution mass spectrometer or quantitative analysis using a high-sensitivity mass spectrometer, it cannot be said to satisfy all requirements because of the instrument's high cost and difficulty of operation, meaning it requires specialist operators. There is also growing demand for simple mass spectrometers that are easy to use even by operators without experience, primarily in fields such as synthetic research.

DEVELOPMENT OF A COMPACT MASS DETECTOR

Although a powerful analytical tool in the scientific field, the use of mass spectrometers is not widespread. In the high-performance liquid chromatography (HPLC) market, mass spectrometry was only recently added in the Japanese Pharmacopoeia as a testing method, and there is growing demand for mass spectrometry even among general HPLC users, primarily in the field of pharmaceutical manufacturing. In the HPLC market, however, less than 20% of the more than 200,000 liquid chromatography (LC) systems installed worldwide are connected to a mass spectrometer, and there are high barriers to the adoption of mass spectrometers by HPLC users. Compared to optical detectors for HPLC, the rate of adoption is still very low.

Major reasons for this low rate of adoption include the installation requirements, price, maintenance, and ease-of-operation of mass spectrometers. The Chromaster 5610 MS Detector has enhancements intended to deal with these issues, which act as barriers to adoption by HPLC users, and was developed with the aim of providing new users with a low-cost mass detector that is simple to use (see Fig. 1).

(1) Compact design

The Chromaster 5610 MS Detector has a similar installation footprint to a Chromaster HPLC system, with space being saved by the development of compact and accurate ion optics and the use of a small vacuum pump.

(2) Elimination of special installation requirements

When the Chromaster 5610 MS Detector is used as a liquid chromatography/mass spectrometry (LC/MS) system, the solvent (mobile phase) injected in the stage prior to the mass detector is split by a ratio of between 1/100 and 1/250 and introduced at a rate of only a few microliters per minute. This significantly reduces the amount of solvent that escapes into the environment. It also significantly reduces use of the nitrogen gas required during ionization compared to a conventional mass spectrometer, which makes it possible to use a simpler nitrogen gas supply system. Similarly, rather than the 200-V power supply required

LC: liquid chromatography MS: mass spectrometry
HPLC: high-performance liquid chromatography

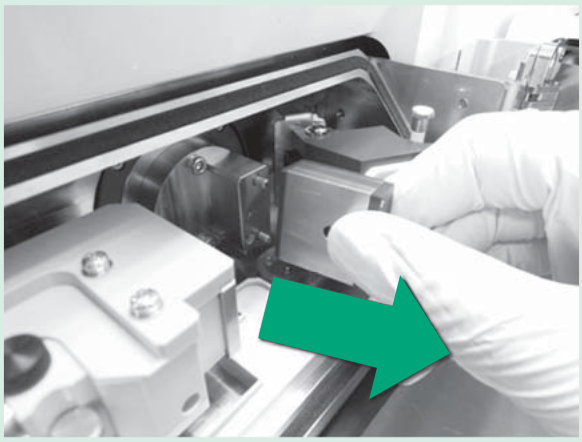
Fig. 1—Chromaster LC/MS System.
The Chromaster LC/MS system combines a Chromaster HPLC system (left) and a Chromaster 5610 MS Detector (right) to enable more reliable analysis.

by a conventional mass spectrometer, the Chromaster 5610 MS Detector can operate on a 100-V supply.

(3) Easier maintenance

Whereas maintenance work cannot typically be performed on a mass spectrometer without releasing the vacuum, the Chromaster 5610 MS Detector uses an atmospheric-pressure ion filter (AIF) as the ion optics filter in its ion injector. Accordingly, routine maintenance involves simply removing, cleaning, and reinserting this filter, without any need to release the vacuum (see Fig. 2). As the ion trajectory makes a right-angle turn inside the AIF, this serves to minimize neutral molecules and contaminating ions from the ion injector. Next, an axial shift chamber at the entrance to the downstream vacuum stage further reduces any remaining contaminating ions, preventing soiling of the electrodes in the interior of the vacuum region.

The aim with the Chromaster 5610 MS Detector is to open up new markets beyond those for large mass spectrometers, with the small size and elimination of installation restrictions making it easier to install the instrument at HPLC laboratories that otherwise lack the right conditions for installing an a mass spectrometer, and by reducing user workload by making maintenance easier.



AIF: atmospheric-pressure ion filter

Fig. 2—Removal of AIF.
Routine maintenance involves merely removing, cleaning, and reinserting the AIF (center).

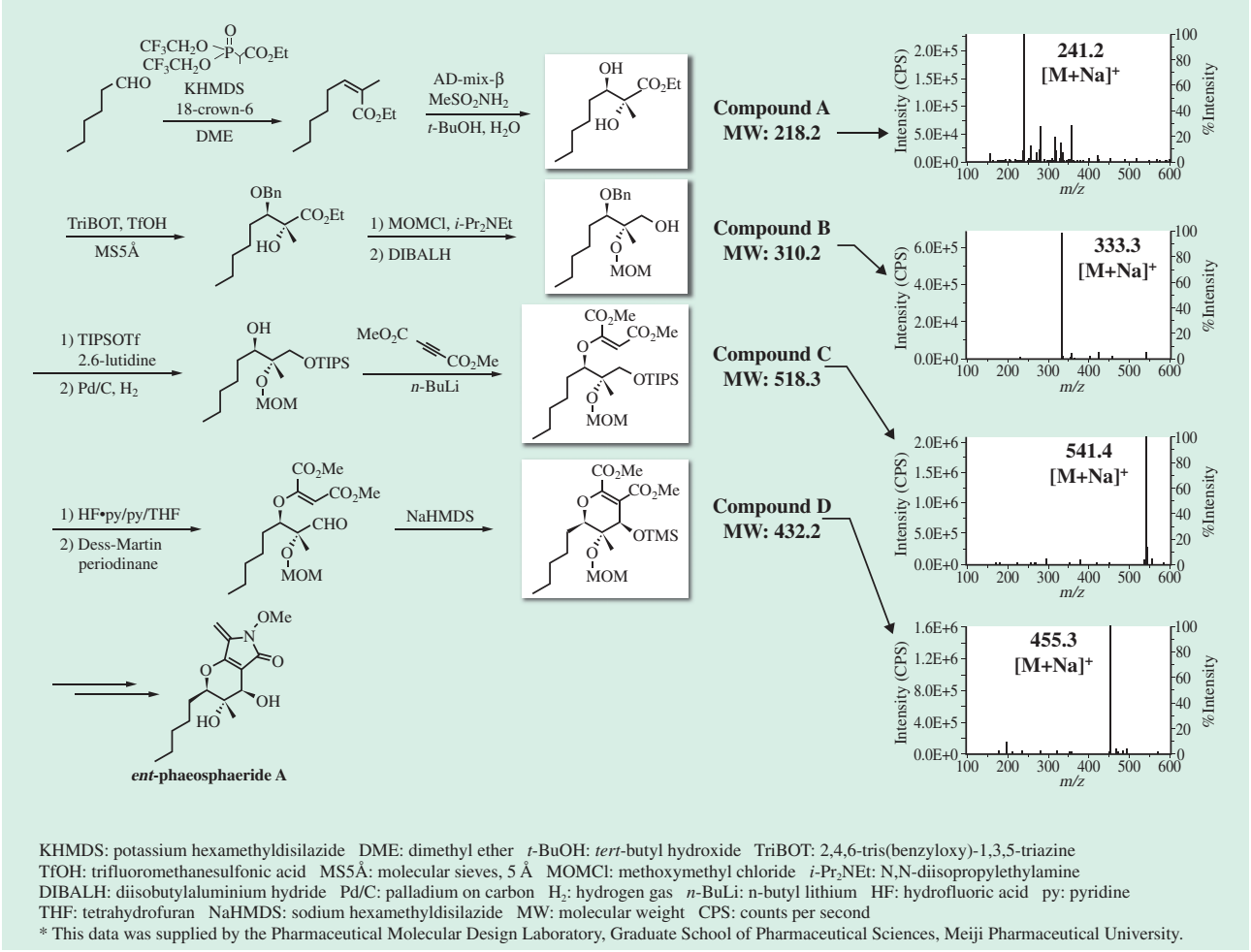
APPLICATIONS IN DRUG DISCOVERY RESEARCH

This section describes the three different configurations in which the Chromaster 5610 MS Detector can be used: as a conventional standalone mass detector used for mass spectrometry (using the direct infusion method), for LC/MS, and for the recently developed thin-layer chromatography-mass spectrometry (TLC-MS) method. It also presents examples from the drug discovery research sector of each of these uses.

Determining Mass Information for Intermediate Products of Natural Product Synthesis[1]

In the total synthesis of natural compounds selected as drug discovery targets, it is necessary to confirm that the desired compounds are being produced at each step of the reaction. The analysis of intermediate reaction products is particularly important in the case of natural compounds with complex structures for which synthesis is also complex. In this case, the Chromaster 5610 MS Detector was used to perform mass spectrometry on four intermediate compounds produced during the total synthesis of phaeosphaeride A, a naturally-occurring compound with anticarcinogenic properties (see Fig. 3).

Table 1 lists the mass spectrometry conditions. The compounds A to D shown in Fig. 3 were each diluted to 10 ppm with methanol and analyzed by the Chromaster 5610 MS Detector using the direct infusion method. In each case, the results indicated the



KHMDS: potassium hexamethyldisilazide DME: dimethyl ether *t*-BuOH: *tert*-butyl hydroxide TriBOT: 2,4,6-tris(benzyloxy)-1,3,5-triazine
TfOH: trifluoromethanesulfonic acid MS5Å: molecular sieves, 5 Å MOMCl: methoxymethyl chloride *i*-Pr_2NEt: N,N-diisopropylethylamine
DIBALH: diisobutylaluminium hydride Pd/C: palladium on carbon H_2: hydrogen gas *n*-BuLi: n-butyl lithium HF: hydrofluoric acid py: pyridine
THF: tetrahydrofuran NaHMDS: sodium hexamethyldisilazide MW: molecular weight CPS: counts per second
* This data was supplied by the Pharmaceutical Molecular Design Laboratory, Graduate School of Pharmaceutical Sciences, Meiji Pharmaceutical University.

Fig. 3—Scheme for Total Synthesis of ent-phaeosphaeride A (left) and Mass Spectra of Intermediate Products A to D (right).
The synthesis of natural compounds involves a large number of reaction steps. Whether or not each step of the synthesis reaction is proceeding correctly can be determined by using a mass detector to analyze the composition of intermediate products.

presence of sodium adduct ions ([M+Na]$^+$). As direct infusion is a very simple technique, involving the injection of the sample using a syringe, it can obtain mass information about the compounds quickly.

TABLE 1. Conditions for Analyzing Intermediate Products of *ent*-phaeosphaeride A Synthesis (Direct Infusion Method)
The table lists the conditions for analyzing the intermediate products of ent-phaeosphaeride A synthesis (by direct infusion).

Ionization method	ESI
Polarity	Positive
Ionization voltage	2,200 V
Measurement mode	Scan
Gas flow rate	0.5 L/min
IS/AIF temperature	70°C/120°C
Syringe pump flow rate	2 µL/min

ESI: electrospray ionization IS: ion source

LC/MS Analysis of Microbial Culture Fluid

HPLC separates the constituents of a sample by utilizing the differences in the affinities (holding force) of their stationary and mobile phases, and detects these using the appropriate detector for the properties of each constituent. While ultraviolet (UV) detectors are widely used, qualitative analysis of the material in this example is performed mainly by holding time, with quantitative analysis being performed by peak intensity and area. Although a diode array detector (DAD) works on the same principle as a UV detector, it can collect three-dimensional chromatogram data due to its ability to obtain spectrum information as well as time axis and peak intensity.

A mass detector can obtain this three-dimensional chromatogram data, made up of time axis, peak intensity, and mass spectrum, through its use in tandem with HPLC (see Fig. 4).

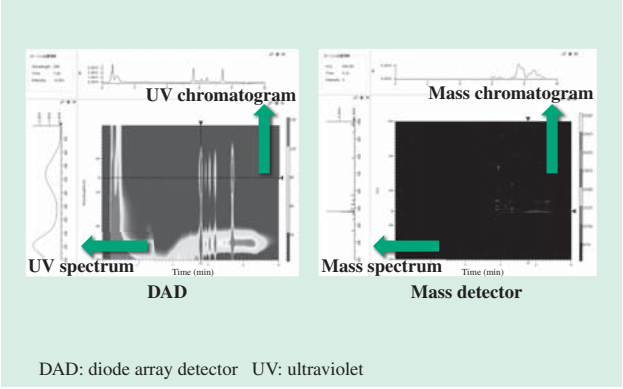


Fig. 4—Contour Maps Showing DAD and Mass Spectrometry Data from Analysis of Microbial Culture Fluid.
Presenting the data as contour lines enables the three-dimensional display of time axis, peak intensity, and mass information, providing a comprehensive overview of the results. This function, which is used routinely for DAD data, is also available for mass spectrometry data on the Chromaster 5610.

Using a DAD only, it is not possible to perform an analysis of compounds without UV absorption in the case of samples that contain a large number of different components, such as a mixture of different compounds in solution. It can also be more difficult to identify the composition because the DAD output is easily influenced by the mobile phase or differences in the concentration of the compounds in solution. When using a mass detector, on the other hand, there are also cases when it is difficult to detect components that are not easily ionized and to identify compounds that have the same mass. The following describes an example analysis that uses two detectors with different characteristics to overcome these problems.

The screening of biologically active compounds found naturally in sources such as microorganisms and plants is a traditional method for discovering lead compounds with the potential to become targets for drug discovery. Even now, however, when high-throughput screening is becoming a mainstream technique, its importance is being reappraised[(2)], with high-throughput screening meaning the artificial synthesis of large numbers of different types of new compounds and the isolation of their active components. The example described here involves screening microbial culture fluid for valuable compounds using an LC/MS system that combines a Chromaster 5610 MS Detector and a DAD. Tables 2 and 3 list the analysis conditions.

As shown in Fig. 4, the mass spectrometry data from the Chromaster 5610 is presented using contour lines in the same way as the DAD measurements. While the resulting data is very complicated in the case of samples, such as microbial culture fluid, that contain large numbers of compounds, presenting it in three-dimensional form helps visualize the change in each measurement.

Fig. 5 shows the UV spectra and mass spectra for peaks (1) to (3) detected at a UV wavelength of 324 nm. Whereas the UV spectra show three similar patterns, the mass spectra are completely different, indicating that the three peaks represent different compounds. While the components in this case are suited to mass spectrometry, UV analysis works better for compounds that are not easily ionized. In this way, samples containing a large number of different components can be analyzed by making complementary use of the UV and mass spectrum data.

Mass Spectrometry Using TLC-MS Interface

TLC is a type of chromatography that works by placing spots of a mixture on a glass or other plate coated with a thin film of an adsorbent such as silica gel or alumina and then allowing a solvent to act on it. It is widely used in synthetic research and other research as a simple, low-cost method for separating and analyzing the components of a mixture.

The use of mass spectrometry to identify the components of a sample separated by TLC used to take a lot of effort, involving (1) scraping the separated

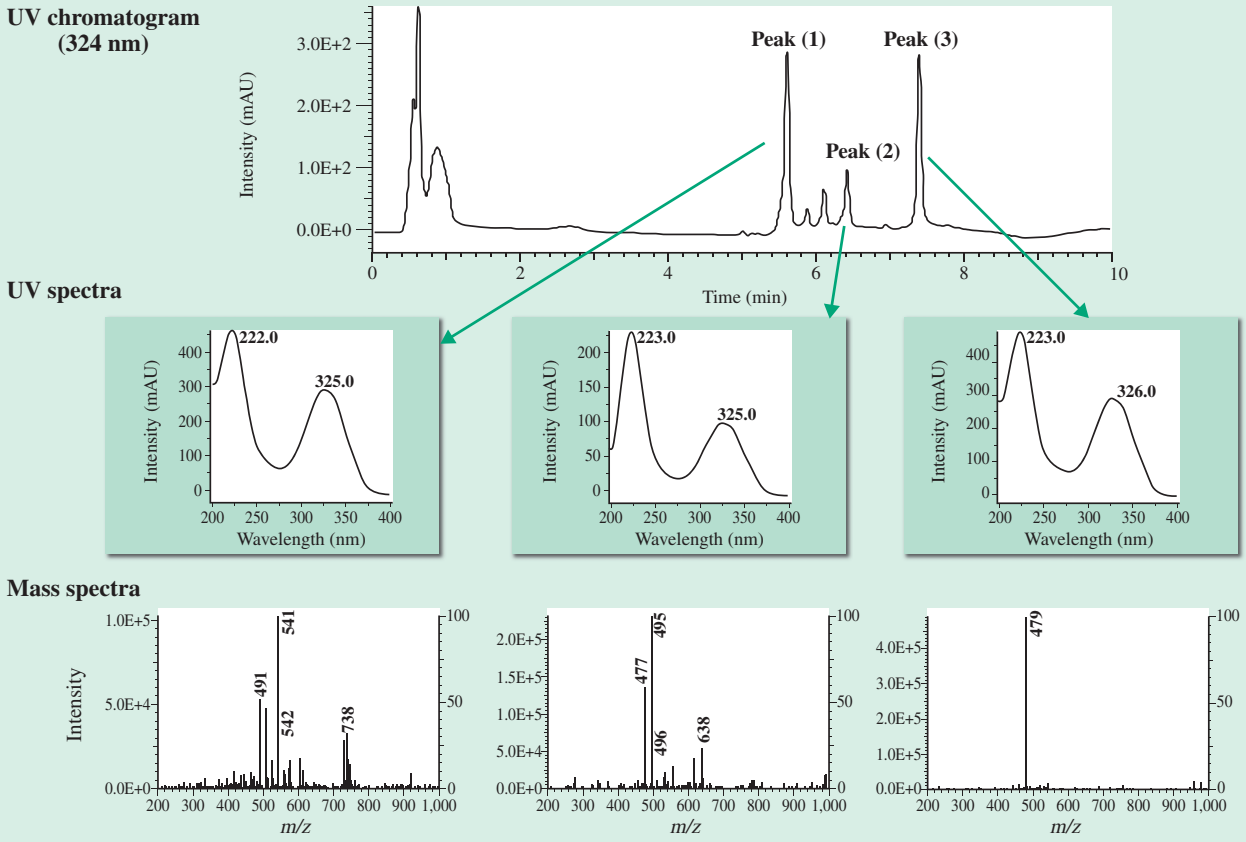
TABLE 2. Experimental Conditions of MS Detector for Analysis of Microbial Culture Fluid (LC/MS Analysis)
The table lists the experimental conditions of an MS detector for an analysis of microbial culture fluid (LC/MS analysis).

Ionization method	ESI
Polarity	Positive
Ionization voltage	2,700 V
Measurement mode	Scan: (*m/z* 200-400)

TABLE 3. Experimental Conditions of HPLC for Analysis of Microbial Culture Fluid (LC/MS Analysis)
The table lists the experimental conditions of HPLC for an analysis of microbial culture fluid (LC/MS analysis).

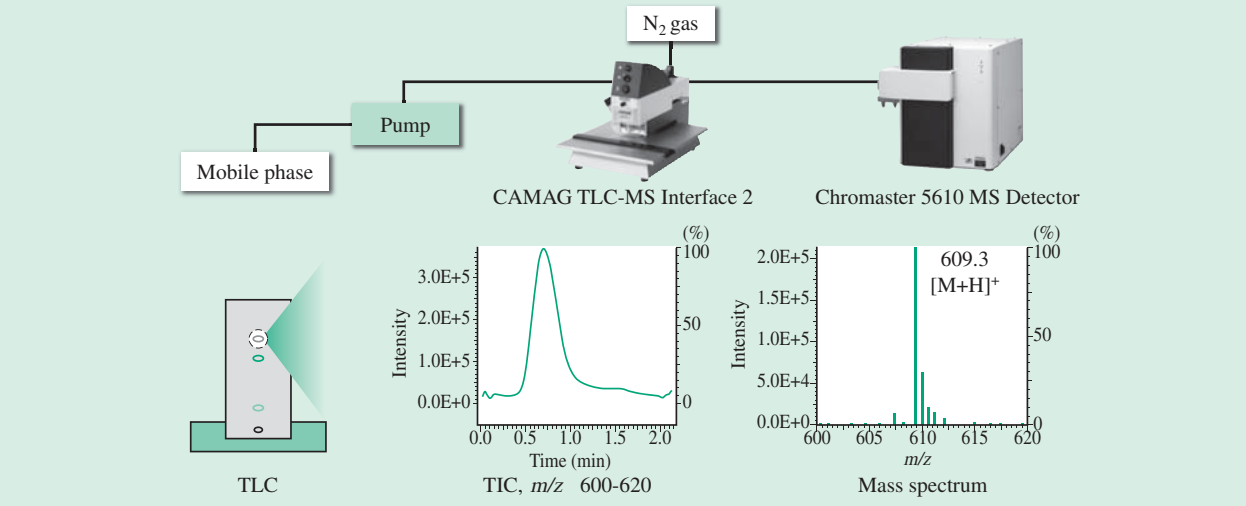
Column	LaChromUltra II (1.9 µm) 2.0 mm I.D.×50 mm
Mobile phase	A: 0.1% HCOOH in H_2O (v/v) B: 0.1% HCOOH in CH_3CN (v/v) %B=20 (0-0.5 min)-100 (3-5 min)-20 (5.1-10 min)
Flow rate	0.2 mL/min (split ratio: 1:50)
Injection amount	20 µL

I.D.: internal diameter v/v: volume per volume



mAU: absorbance unit
* This data was obtained with the cooperation of the Laboratory of Microbial Chemistry, Graduate School of Pharmaceutical Sciences, Kitasato University.

Fig. 5—Identification of Composition of Peaks Separated from Microbial Culture Fluid.
Identification can be difficult, as in this example, because the UV spectrum is easily influenced by the mobile phase and the compounds in the solution. In such cases, the reliability of identification can be improved by also obtaining the mass spectrum to clarify the differences between components.



N_2: nitrogen TLC: thin-layer chromatography TIC: total ion chromatogram

Fig. 6—System Configuration of Online TLC-MS System.
Mass information can be obtained in only one or two minutes by extracting the material directly from the spots on the TLC plate and performing online injection into the mass detector.

TABLE 4. Experimental Conditions of MS Detector for TLC-MS Analysis
The table lists the experimental conditions of an MS detector for TLC-MS analysis.

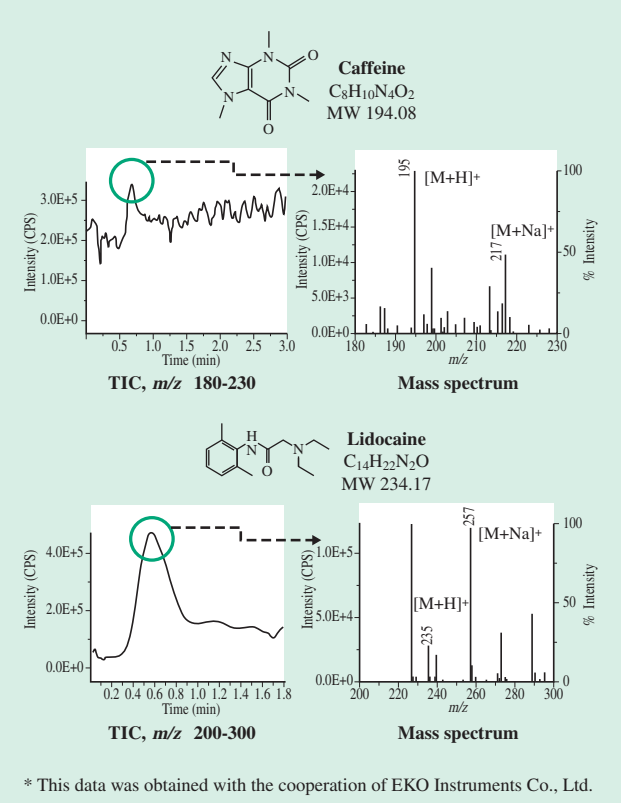
Ionization method	ESI
Polarity	Positive
Ionization voltage	2,600 V
Measurement mode	Scan

TABLE 5. Pump Settings for TLC-MS Analysis
The table lists the pump settings for TLC-MS analysis.

Mobile phase	Methanol
Flow rate	0.1 mL/min (split ratio: 1:50)

spots, (2) extracting them, and (3) analyzing them in a mass spectrometer. Recent years, however, have seen the availability of techniques for extracting the spots directly from the plate followed by online injection into the mass spectrometer (as shown Fig. 6), which have significantly simplified composition analysis. In this example, online TLC-MS analysis is performed by a CAMAG TLC-MS Interface 2 (CAMAG) and Chromaster 5610 MS Detector. Tables 4 and 5 list the analysis conditions.

Fig. 7 shows mass spectrometry data for caffeine and lidocaine obtained by TLC. Here, 2 µL each of caffeine and lidocaine in methanol solution (equivalent to 200 ng) was separated on a TLC plate and the components were extracted using a solvent (methanol) delivered via a pump by applying an extraction piston to the spots. The extracted fluid was transferred immediately to the Chromaster 5610 MS Detector and the mass data shown in Fig. 7 was obtained in one to two minutes. In this way, components separated using TLC can be identified quickly.



* This data was obtained with the cooperation of EKO Instruments Co., Ltd.

Fig. 7—Analyses of Caffeine (top) and Lidocaine (bottom) Using TLC-MS System.
Caffeine and lidocaine equivalent to 200 ng can be detected by extracting the material directly from the spots on the TLC plate.

CONCLUSIONS

This article has described three example applications for the compact Chromaster 5610 MS Detector: the analysis of the intermediate products of synthesis using the direct infusion method, the screening of microbial culture fluid using LC/MS, and the analysis of a mixture using TLC-MS.

There remains considerable unmet demand for this type of laboratory-level analysis using a simple mass detector and Hitachi High-Tech Science Corporation intends to continue supplying solutions to satisfy customer needs.

ACKNOWLEDGMENTS

Research data from the Pharmaceutical Molecular Design Laboratory of the Graduate School of Pharmaceutical Sciences at Meiji Pharmaceutical University and the Laboratory of Microbial Chemistry of the Graduate School of Pharmaceutical Sciences, Kitasato University School of Pharmacy was used in preparing this article. The authors would like to take this opportunity to express their deep gratitude.

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Featured Articles

Rapid Detection and Element Identification of Fine Metal Particles for Underpinning Battery Quality

—X-ray Particle Contaminant Analyzer EA8000—

Tsuneo Sato
Yoshiki Matoba

OVERVIEW: Along with measures for reducing the load on the environment, development of fuel cells and electric vehicles using rechargeable batteries has proceeded with the aim of reducing CO_2 emissions. For the LIBs, fuel cells, and other components used for this purpose, greater safety and quality is required particularly in automotive applications. Metal particle contamination in batteries is one cause of degrading reliability and quality, making this an important aspect of quality control. To satisfy this new demand, Hitachi High-Tech Science has developed X-ray technology and equipment to detect and identify fine metal particles.

INTRODUCTION

USE of technologies such as lithium-ion rechargeable batteries (LIBs) and fuel cells is growing in a variety of fields to help reduce the load on the environment. However, the presence of metal particle contaminants in LIBs and fuel cells is a cause of decreased safety and performance. For this reason, controlling metal particles in the manufacturing process is important for maintaining product safety and performance. These metal particles are also a cause of decreased manufacturing yield. With the growing use of LIBs and fuel cells in automotive applications over recent years, dealing with metal particles is seen as particularly important. So, battery manufacturers have adopted a variety of measures for quickly identifying metal particle contamination in order to maintain battery quality and yield.

To overcome these challenges, Hitachi High-Tech Science Corporation released an X-ray particle contaminant analyzer (the EA8000) for detecting metal particles and analyzing their composition (see Fig. 1).

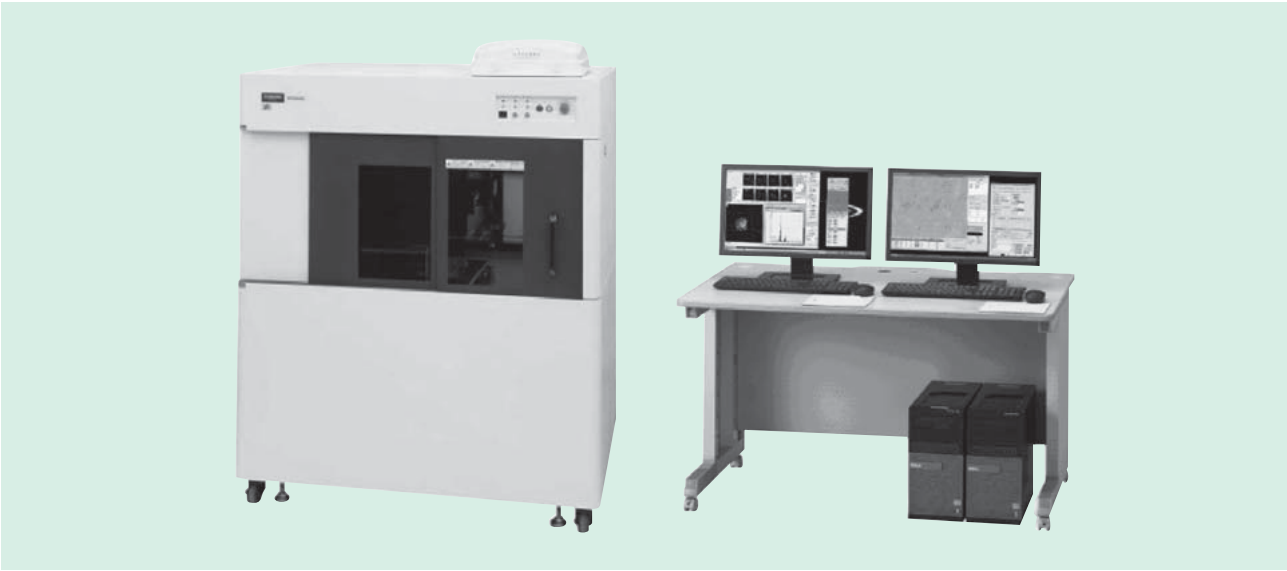

Fig. 1—X-ray Particle Contaminant Analyzer EA8000.
The photograph shows the EA8000 developed by Hitachi High-Tech Science Corporation.

This article describes the EA8000 and some example measurements with particular reference to the control of metal particles in LIB manufacturing.

RAPID DETECTION AND ELEMENT IDENTIFICATION OF FINE METAL PARTICLES

Customer Requirements, Existing Techniques, and Associated Challenges

LIB manufacturing sites need a way to detect contamination by metal particles in materials or intermediate processes. For example, there is a requirement for the detection of metal particles of 20 µm or more in the cathode plates of A4-size LIBs, and the rapid analysis of their number, size, and composition. In some cases, the requirements include detection and analysis of internal as well as surface contaminants.

One method for determining the level of contamination and particle composition is inductively coupled plasma (ICP) analysis*1. Unfortunately, this method cannot distinguish between cases with a large number of sub-micron particles and those with a single large contaminant with potential to cause performance degradation and heat generation. Similarly, it is difficult to detect internal metal particles using scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX)*2 because the electron beam only penetrates a few micrometers into the sample surface.

X-ray fluorescence (XRF) analysis identifies elements using the secondary (fluorescent) X-rays generated when a material is exposed to X-rays. µXRF, in which the analysis is performed over a very small area, obtains an element map that can be used to determine the number, size, and composition of metal particles near the surface and in the interior. Unfortunately, µXRF is impractical because scanning over the entire surface of a sample to detect fine metal particles can take 10 hours or more just to identify particles on the surface, with even more time being required to identify particles in the interior.

Features of the EA8000

The EA8000 uses X-ray transmission imaging, which takes advantage of the differences in the X-ray transparency of different materials to detect fine metal particles in a short amount of time. Hitachi High-Tech Science has also developed an element mapping system that uses XRF with increased sensitivity in a minute area to analyze the contaminants. By mounting both of these on the same XYZ stage, the system can rapidly detect metal particles on the order of 20 µm over an A4-size area and perform element identification(1) (see Fig. 2).

*1 A type of emission spectrochemical analysis that is widely used for the analysis of inorganic elements. Samples are put in solution and the type and quantity of the elements they contain are determined by spectrochemical analysis using plasma.

*2 An instrument that observes a sample using a scanning electron microscope (SEM) while at the same time performing an elemental analysis based on the distinctive X-rays emitted by the sample in response to the electron beam. It can be used to obtain a two-dimensional element mapping images.

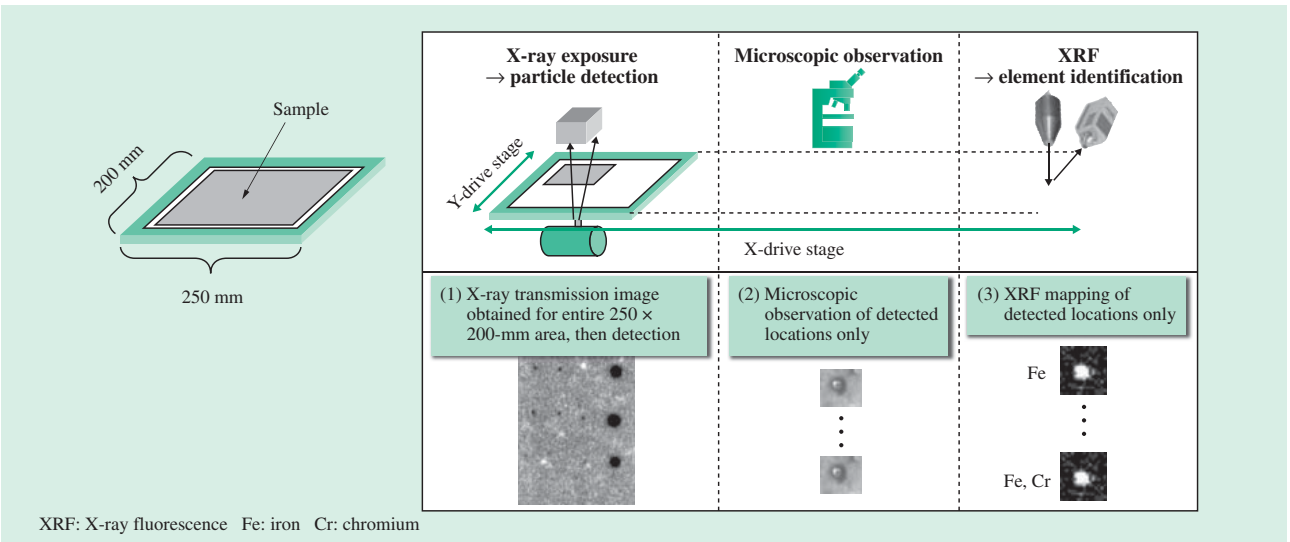

Fig. 2—Sequence of Steps in EA8000 Measurement.
(1) Particle detection, (2) microscopic observation, and (3) element identification can all be performed automatically with the sample on the same stage.

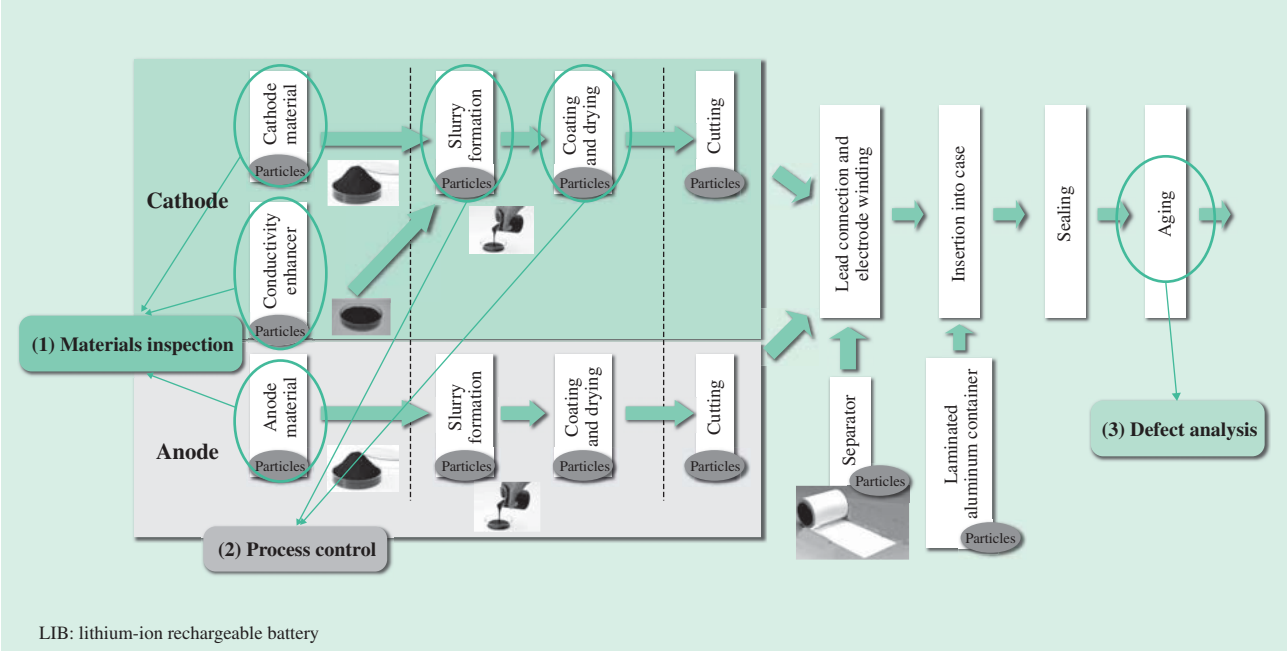

Fig. 3—LIB Manufacturing and Suitable Applications for EA8000 Analysis.
There are applications for the EA8000 at various stages in the LIB manufacturing process.

X-ray transmission imaging

Different materials have different X-ray transparency. Metal, for example, has low X-ray transparency compared to plastic. If metal particles are present in plastic, they appear as dark shadows in an X-ray transmission image. The location of these can then be determined by image processing.

Hitachi High-Tech Science developed an X-ray transmission imaging system for the EA8000 that achieves high spatial resolution and high sensitivity through enhancements such as optimization of the X-ray detector, enabling it to rapidly detect metal particles on the order of 20 µm. The time taken to perform detection ranges from several minutes up to around 20 minutes (depending on the type of sample).

Element identification by XRF

The XRF analysis of contaminants is able to identify their elemental composition quickly by only performing XRF mapping for those locations where contaminants were detected in the X-ray transmission image.

To make the analysis faster, XRF analysis also incorporates an X-ray system with a polycapillary lens that makes the beam sharper and more intense, and a silicon drift detector (SDD) with excellent count rate performance (number of X-rays that can be counted per unit of time). Thanks to these features, it takes only one to three minutes to perform element identification of detected fine metal particles.

EXAMPLE ANALYSES USING EA8000

Fig. 3 shows an overview of how LIBs are manufactured. The EA8000 is suitable for analytical work in the materials inspection, process control, and defect analysis steps within this process. This chapter presents measurement examples using simulated samples from these three applications.

Materials Inspection (Carbon-based Powder Measurement Sample)

To provide an example of materials inspection, measurements were performed on a sample of carbon-based powder of the sort used in anodes and to enhance conductivity.

Commercially available graphite was used for the sample. As shown in Fig. 4 (a), the measurement was performed on graphite placed in a zippered polythene bag that was spread out over a 250 × 200-mm area.

The measurement took approximately 13 minutes to obtain an X-ray transmission image, and XRF mapping was performed at locations where material was detected in this image, taking 50 seconds per location (see Fig. 4).

Fig. 4 (b) shows the transmission image of the entire bag. Variations in thickness are visible depending on the amount of graphite powder present at different places. Fig. 4 (c) shows an enlargement of one such region in which a location is visible that is

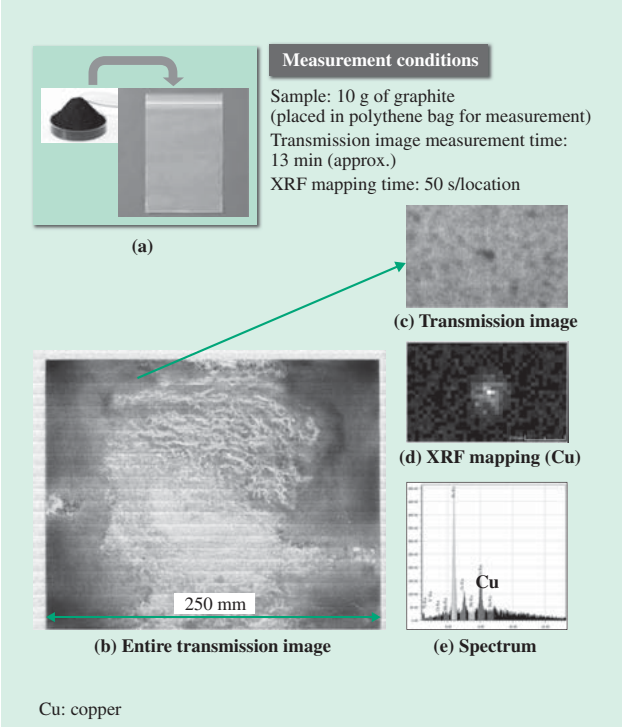

Fig. 4—Example Analysis of Carbon-based Powder Sample.
Carbon-based powder can be measured with just simple sample preparation.

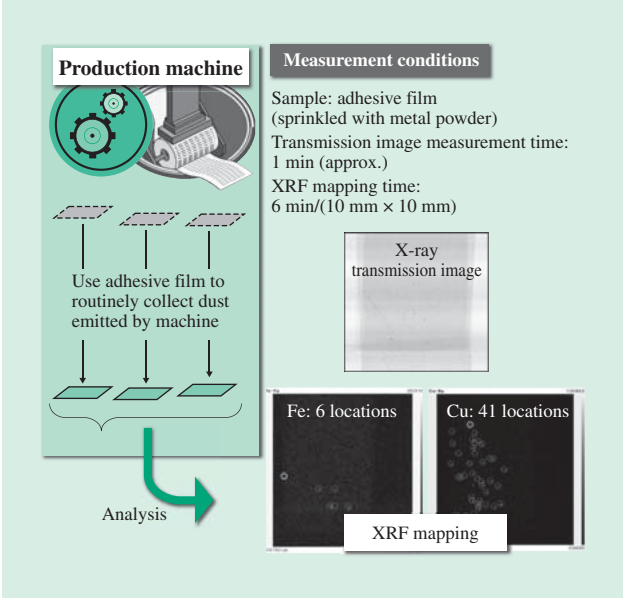

Fig. 5—Example Analysis of Sample for Dust Emitted by Production Machinery or Other Sources.
Analysis can determine the elemental composition, number, and size of metal particles adhering to adhesive film.

darker than its surroundings. The size of this particle is approximately 100 μm. Locations like this can be identified by image processing. XRF mapping of the particle indicates that it is made of copper (Cu) [see Fig. 4 (d) and (e)].

This technique can perform measurements on carbon powder with only simple sample preparation and, in doing so, can prevent loss of quality or yield by quantifying the presence of large contaminants with sizes in the tens of micrometers range that have the potential to cause defects.

Process Control (Measurement Results for Dust-generated Particle Control Technique)

As an example of use in process control, this section describes a measurement for dealing with dust emitted by production machinery or other sources.

Placing adhesive film next to a production machine and routinely taking it away for measurement provides a way to identify problems such as a deterioration in the condition of the machine that is accompanied by a sudden increase in the amount of dust it emits. To simulate this situation, a measurement was performed on an adhesive film that had been sprinkled with metal powder. XRF mapping for particular elements [iron (Fe) and Cu] was performed over the entire surface of the film and the number of such particles was counted (see Fig. 5). Note that this could also be performed by taking measurements at the particle locations identified in the X-ray transmission image.

This method provides a simple way to determine the elemental composition of the particles, and it can be used to monitor for problems in a production machine based on the trend in the amount of dust it emits.

Defect Analysis (Sample for Analysis of Separator)

As an example of defect analysis, this section describes a measurement that might be used in the analysis of particles in and particles adhering to the surface of a separator.

The sample was created by sprinkling stainless steel (SUS) powder on polyethylene terephthalate (PET) film with a thickness of 100 μm.

The measurement took approximately four minutes to obtain a transmission image of the 250 × 200-mm area, and XRF mapping took approximately 40 seconds per location (see Fig. 6).

A particle was detected at the edge of Fig. 6 (a). The measurement found a coin-shaped SUS particle with a known diameter of 20 μm at the top right of Fig. 6 (a). Fig. 6 (b) to (d) show the analysis results for this particle. The particle is visible in the transmission image [Fig. 6 (b)], and the Fe mapping [Fig. 6 (c)] shows a high intensity for Fe at that location,

indicating that Fe is present. Fig. 6 (d) shows the spectrum from the center of the particle. Although the measurement was completed in a short amount of time (approximately 40 seconds), it shows peaks for Fe, chromium (Cr), and nickel (Ni).

This demonstrates how the EA8000 can perform automatic measurements of tiny amounts of material, and that it can conduct defect analyses that are automatic (with minimal variation due to the operator performing the test) to identify particles that may have escaped by physical action from a separator.

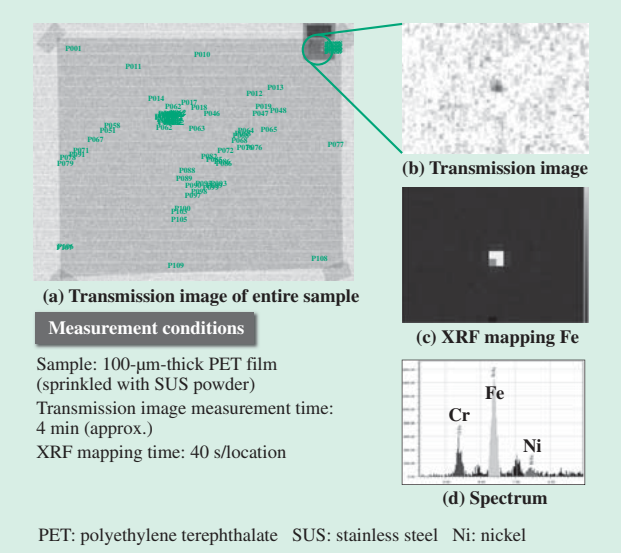

Fig. 6—Defect Analysis Sample for Analysis of Separator. (a) shows the full transmission image of the sample sprinkled with SUS powder, and (b), (c), and (d) show the analysis results for a particle of known size.

BENEFITS OF USING EA8000

The following summarizes the benefits that can be obtained at LIB manufacturing sites by performing the measurements described in the chapter above.

(1) Increases in defect rates can be prevented by performing materials inspection to quantify the presence of large particles with the potential to cause defects.

(2) Monitoring of production machinery for abnormal conditions can be performed by regularly checking coated electrodes or dust emission by machines. It is also possible to determine the scope of any problems that occur in order to minimize the number of batteries that are rejected.

(3) Defect analysis can be performed automatically, with minimal variation due to the operator performing the test. There is also potential for determining defect causes that could not be identified in the past.

CONCLUSIONS

The market for LIBs and similar products is growing. This article has described examples of how the EA8000 can be used to deal with problems associated with the production of these products, and the associated benefits.

Hitachi High-Tech Science intends to draw on the knowledge it gained in the development of the EA8000 to develop inline models that are capable of higher throughput and utilize them in other fields.

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Featured Articles

Coating Thickness Measurement with High-performance for Latest Electronic Fine Components of Mobile Devices

—FT150 Series Fluorescent X-ray Coating Thickness Gauge—

Haruo Takahashi
Masaki Izumiyama
Ryusuke Hirose, Dr. Eng.
Toshiyuki Takahara

OVERVIEW: X-ray fluorescence analysis is widely used for measuring the coating and plating film thickness of electronic components and other products as it can perform non-destructive and non-contact simultaneous measurement of multi layer coatings. As the components to be measured become increasingly scaled-down, the X-rays used for this purpose need to be tightly focused. The FT150 series high-performance fluorescent X-ray coating thickness gauge meets this requirement. It realizes nanometer-level plating thickness measurement over an area of several tens of microns, by using polycapillary X-ray focusing devices, in place of the conventional collimator method, thereby increasing the intensity of X-rays to which the sample is exposed by around 1,000 times. This article introduces some typical applications to describe the measurement precision performed by the FT150 series.

INTRODUCTION

X-RAY fluorescence analysis uses the fluorescent X-rays emitted from a sample by irradiating incident X-rays, and can perform non-destructive and non-contact measurement of the quantities of each element present in the measurement region. Utilizing this capability, the technique is widely used for measuring plating thickness. One important application for fluorescent X-ray plating thickness measurement is the plating thickness measurement of terminal parts such as electronic components, printed circuit boards, and connectors. As the plating of these terminals is an important technology for ensuring the reliability of electrical connections between components, it is routinely measured at production plants.

As electronic devices become smaller and lighter, so too are the components they use becoming smaller and more densely mounted, with the result that there is growing demand for the ability to measure plating thicknesses over areas of 100 μm or less.

Gold (Au) is commonly used as a plating for electronic components because of its excellent electrical and chemical characteristics. Au plating is expensive and is a critical factor in quality, so it is becoming increasingly important to control plating thickness. Recent years have seen numerous examples of plating thicknesses of 10 nm or less, and sites that deal with plating thickness control for the latest electronic components are demanding instruments that can easily and accurately measure platings with nanometer-level thicknesses over areas of a few tens of micrometers.

FT150 SERIES

Hitachi High-Tech Science Corporation developed the FT150 series high-performance fluorescent X-ray coating thickness gauge, which features simple operation and provides precision measurement of plating thickness processes at electronic component manufacturing plants. Fig. 1 shows a photograph of the instrument.

Product Range

The FT150 series is made up of three models with different combinations of sample chamber and polycapillary to suit different measurement applications (see Table 1). The X-ray irradiating system consists of an X-ray tube as X-ray source and a polycapillary X-ray focusing device and is available in a version that is optimized for nickel (Ni), palladium (Pd), or Au, especially for very thin, 50nm or less, thicknesses, another version that is suitable for a wider range of

Fig. 1—Exterior of the FT150.
From the left, the photographs show the exterior of the measurement head, stage controller, and PC used for operation.

plating materials, including tin (Sn), silver (Ag), and for comparatively thick Pd or Au. The sample chamber is available in two sizes: the standard size of 300 mm × 400 mm, and a larger option specialized for large 600-mm-square printed circuit boards (see Fig. 2).

X-ray Irradiation System and Detection Intensity

The X-ray irradiation system in the FT150 series uses a polycapillary X-ray focusing device that enables precision measurement by focusing high-intensity X-rays on a very small area. The polycapillary on the FT150 and FT150L, which is optimized for thin Pd and Au platings, has a beam diameter of 30 μm for Au platings, while that on the FT150h has a beam diameter of 35 μm for Sn platings.

The FT150 series has also been optimized for X-ray detection sensitivity, using a silicon drift detector (SDD) that is able to withstand high X-ray intensities without saturating. Used in combination with the polycapillary X-ray focusing device, the FT150 and FT150L achieve two times higher Au X-ray fluorescence (XRF) intensity than conventional models, while the FT150h can perform measurements in the 20-keV+ range, which has traditionally been difficult to detect.

Ease of Operation

As fluorescent X-ray plating thickness gauges are used regularly at manufacturing plants, it is important that they be easy to use.

The FT150 series models were designed for ease-of-operation based on the following three concepts.
(1) Large samples can be easily set in the sample chamber because of its large space
(2) Easy to open and close with little force
(3) No structural parts located where they will obstruct the view of the measurement position

TABLE 1. FT150 Series Product Range
Three models are available with different combinations of polycapillary and sample chamber.

	Sample chamber	Polycapillary
FT150	Standard	Characteristics suitable for thin Ni/Pd/Au platings
FT150L	Large	"
FT150h	Standard	Characteristics suitable for Sn and Ag platings

Ni: nickel Pd: palladium Au: gold Sn: tin Ag: silver

Fig. 2—FT150L with Sample Chamber Door Open.
The large sample space provides ample room for large flexible samples.

To prevent radiation leakage, the FT150L designed for the measurement of large printed circuit boards has a cover large enough to hold these large boards instead of the commonly used slit arrangement. In addition to a large door with a power-assisted hinge that is easy to open and close with one hand, the large space above the sample stage reduces the risk of scratching the sample, something that can happen when inserting it into slits (see Fig. 2).

To reduce operator workload, the FT150 series is also equipped with built-in calibration samples. It performs a warm-up run and periodical calibration automatically, without any user instructions.

PRINCIPLES AND FEATURES OF FLUORESCENT X-RAY PLATING THICKNESS MEASUREMENT

Overview of Fluorescent X-ray Plating Thickness Measurement

A sample exposed to primary X-rays in turn emits fluorescent X-rays with energies that are distinctive of the different elements contained in the plating material. As the amount of fluorescent X-rays emitted depends on the thickness of the plating on the sample,

this thickness can be calculated from the fluorescent X-ray intensity. This technique is suitable for use in manufacturing plants because the exposure of the sample to X-rays and their detection are both achieved without contact with the sample plating (see Fig. 3).

In principle, the amount of fluorescent X-rays generated has a degree of statistical variation. Although impossible to eliminate, the relative amount of this variation can be reduced by increasing the number of X-ray photons detected. In other words, precise measurement is achieved by increasing the intensity of primary X-rays and by detecting more of the fluorescent X-rays by improving detector efficiency.

Techniques for Measuring Minute Areas

Fluorescent X-ray plating thickness measurement does not work correctly if the primary X-rays are irradiated outside of the measuring area. This means that the primary X-rays must be shaped into a narrow beam that matches the sample. Although X-rays are a form of electromagnetic radiation, just like visible light, they have a much lower refractive index and this makes it impossible in practice to focus them using an optical lens. A simple and common method for making a narrow X-ray beam is to use a collimator. A small aperture in a metal plate that is thick enough to block the X-rays, only allows X-rays to pass through the target area. Unfortunately, as the X-ray beam is made narrower, its intensity falls roughly in proportion to the area of the hole. As noted above, this degrades the measurement accuracy. Accordingly, the FT150 series models are equipped with polycapillary X-ray focusing devices so that they can expose small areas to high-intensity X-rays. A polycapillary uses total reflection on the inner surface of a hollow glass tube to guide the X-rays and achieve a focusing effect by orienting each individual glass tube so that they are directed at the same point (see Fig. 4).

The polycapillary focusing devices used on the FT150 can focus X-rays that excite Au fluorescence within a 30-μm region (see Fig. 5). The resulting

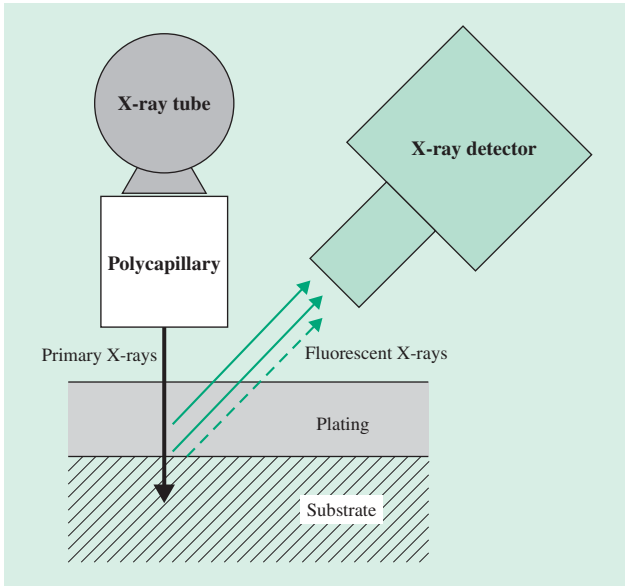


Fig. 3—Principles of Fluorescent X-ray Plating Thickness Measurement.
Non-destructive and non-contact measurement can be performed by detecting the fluorescent X-rays emitted by a sample exposed to primary X-rays.

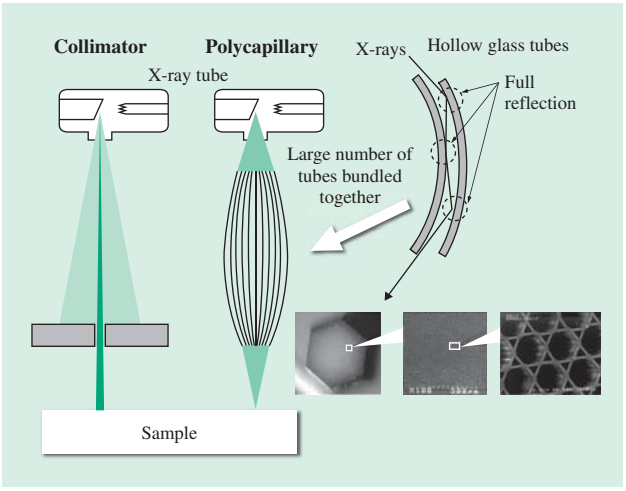


Fig. 4—How Collimators and Polycapillaries Work.
When a collimator is used to produce a narrow beam, most of the X-rays do not reach the sample, resulting in very low intensity. Because a polycapillary focuses the X-rays, it can deliver high intensities.

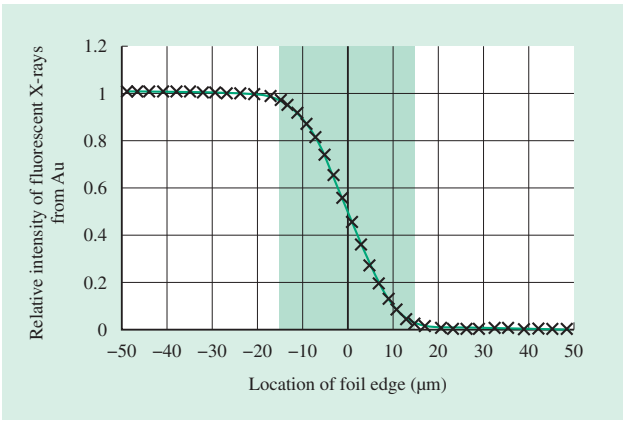
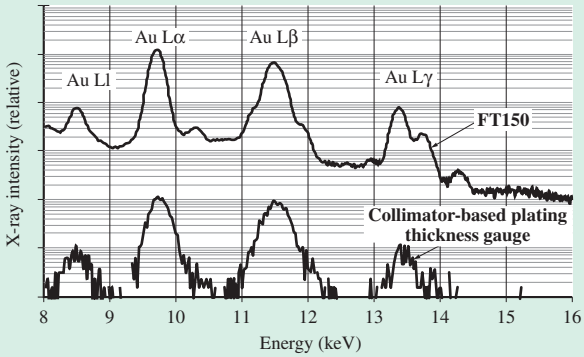


Fig. 5—FT150 Beam Diameters.
The graph plots the change in X-ray intensity as the beam is scanned across the edge of the Au foil. The size of the region of gradual change in intensity indicates that the beam diameter is 30 μm.



Mo: molybdenum W: tungsten
* The FT150 has a tube with an Mo target, 45 kV 1,000 µA, and beam diameter of 30 µm. The collimator system has a tube with a W target, 50 kV1,500 µA, and beam diameter of 90 µm.

Fig. 6—Comparison of Fluorescent X-ray Intensity on FT150 and Collimator-based Plating Thickness Gauge.
The graph plots the spectra measured by each instrument for a bulk sample of Au. The fluorescent X-ray intensity on the FT150 is roughly 1,000 times that of the collimator-based plating thickness gauge.

intensity of fluorescent X-rays from the sample is about 1,000 times greater than that achieved by conventional instruments equipped with a collimator (see Fig. 6).

As this means that even very small areas can be exposed to high-intensity X-rays, a weak X-ray signal from a 1-nm Au layer can be distinguished from the background with only a 30-s measurement.

EXAMPLE MEASUREMENTS

The following chapter presents examples of using the FT150 for measuring two common types of samples: a lead frame and a compact multilayer ceramic capacitor.

Cu/Ni/Pd/Au Three-layer Plating

The FT150 was used to measure a three-layer Ni/Pd/Au plating on the lead frame used for an integrated circuit (IC). The measurement used a stack of Au, Pd, and Ni foil of known thicknesses on a copper (Cu) substrate as a reference.

Ten 100-s measurements were performed and the mean and relative standard deviation (RSD) were obtained. The results demonstrate the ability of the FT150 to perform highly accurate measurements of even thin platings of 10 nm (0.01 µm) or less (see Table 2).

Multilayer Ceramic Capacitor

This example involves using the FT150h to measure the Ni/Sn plating on the electrodes of a commercially available multilayer ceramic capacitor.

TABLE 2. Results of Repeated Measurements of Ni/Pd/Au Plating on Lead Frame
The table lists the mean and RSD obtained from ten 100-s measurements.

	Mean	RSD
Au	0.0062 µm	1.5%
Pd	0.0180 µm	1.9%
Ni	0.9045 µm	0.1%

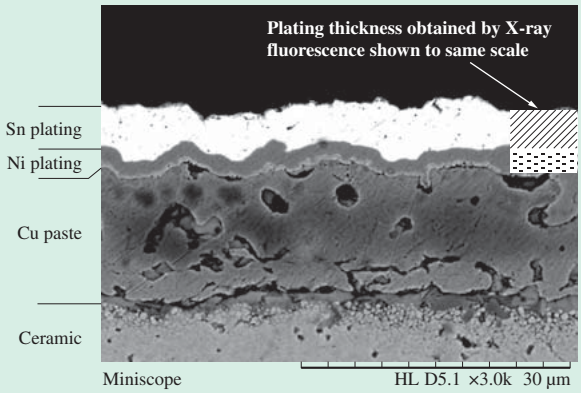
RSD: relative standard deviation

TABLE 3. Results of Repeated Measurements of Ni/Sn Plating on Ceramic Capacitor
The table lists the mean and RSD obtained from ten 30-s measurements.

	Mean	RSD
Sn	4.32 µm	0.4%
Ni	2.46 µm	0.8%

The capacitor's two-layer Ni/Sn plating was measured without any sample preparation. The reference for the measurement was a stack of Sn and Ni foil of known thicknesses on a Cu substrate.

Ten 30-s measurements were taken and the mean and RSD were obtained. The results demonstrate the ability to perform highly accurate measurements with an RSD of 1% or less, despite such a short measurement time (see Table 3).



SEM: scanning electron microscope Cu: copper

Fig. 7—SEM Cross-section of Multilayer Ceramic Capacitor Measured by the FT150.
The plating thickness obtained by X-ray fluorescence is shown to scale at the top right of the SEM image. The results indicate good agreement.

Using a polishing machine, a cross-section of the capacitor was made. After cleaning the cross-section using an ion milling machine, the thickness of the Ni/Sn layer was observed by a scanning electron microscope (SEM), the plating thickness showed excellent agreement with that obtained by X-ray fluorescence (see Fig. 7). The ability of the FT150 to use X-ray fluorescence to make fast and accurate measurements of mean plating thickness over a small area exposed to X-rays enables non-destructive measurement without the need to prepare a cross-section. This makes it suitable for use in the control of plating thickness at manufacturing plants.

CONCLUSIONS

This article has described the rising demand for ways to measure very thin platings over small areas to enable control of the plating thickness of electronic components. It has also presented actual measurement data to demonstrate that the required measurement performance has been achieved by developing a measurement system based on the use of a polycapillary X-ray focusing device to provide a narrow, high-intensity X-ray beam.

Anticipating continued strong demand for scaled-down electronic components with a high level of added value, Hitachi High-Tech Science intends to continue development so that plating thickness measurement, too, can achieve smaller sizes and higher precision.

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Featured Articles

Ultrasonic Imaging of Microscopic Defects to Help Improve Reliability of Semiconductors and Electronic Devices

—Scanning Acoustic Tomograph—

Kaoru Kitami
Kaoru Sakai
Takashi Tomita
Kazuyoshi Kurosawa

OVERVIEW: Hitachi Power Solutions' SAT is an instrument that uses ultrasound to nondestructively detect and image defects such as cracks and delamination in semiconductors and other electronic devices. To achieve high inspection image resolution, it uses an acoustic lens to create a focused beam of ultrasound that is transmitted into the object of inspection. As electronic devices become increasingly compact, measurement images need to have higher resolution and definition. To meet these needs, Hitachi Power Solutions' SAT achieves higher resolution by incorporating an instrument that emphasizes the high-frequency components of the ultrasound transmitted to the object of inspection. This improves detectability from the conventional limit of about 2.5 to 4 μm, to 1 to 1.6 μm. And, by incorporating a process that performs deconvolution by considering the intensity distribution of the focused ultrasonic beam that is transmitted, resulting in a 60% improvement in contrast and a higher-definition inspection image.

INTRODUCTION

TODAY'S ever lighter, thinner, and smaller consumer products are resulting in semiconductors and other electronic devices with increasingly complex and scaled-down structures and package formats. A scanning acoustic tomograph (SAT) uses ultrasound to nondestructively detect cracks, delamination, and voids in these electronic devices, which is crucial for ensuring reliability. However, as electronic devices become smaller, measurement images need to have higher resolution and higher definition.

Hitachi Power Solutions Co., Ltd. has developed and manufactured original SATs to meet these market needs. The fourth-generation of the series was released in April of 2015 (see Fig. 1) and supports 5 to 300 MHz probes.

SAT: scanning acoustic tomograph

Fig. 1—Fourth-generation of Hitachi Power Solutions' SAT. The photo shows the fourth generation of Hitachi Power Solutions' SAT (with options attached).

OVERVIEW OF HITACHI POWER SOLUTIONS' SAT

Principles of Ultrasound-based Defect Detection

SATs use differences in acoustic impedance (an indicator of how easily sound passes through a medium) to image defects. As shown in Fig. 2, when ultrasound is transmitted into a specimen containing a layer of medium 1 and a layer of medium 2, reflection and transmission occur at the interface between the layers. The reflected wave intensity (R) is given by equation (1) below.

$$R = \frac{Z_2 - Z_1}{Z_2 + Z_1} I \quad (1)$$

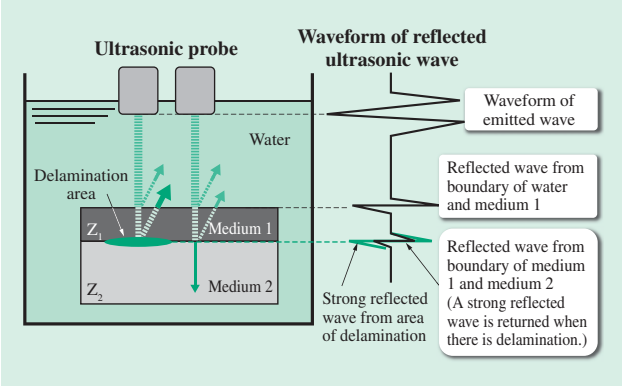

Fig. 2—Principles of Defect Detection Using Ultrasound. The difference in the intensity of the reflected wave from the boundary between medium 1 and medium 2 is imaged by varying gray scale shades.

Here Z_1 and Z_2 are the acoustic impedances of medium 1 and medium 2 respectively, and I is the incident wave intensity. SATs acquire a measurement image by rapidly scanning the ultrasound while displaying its reflected wave intensity or transmitted wave intensity at each point as gray scale shades. The measurement method using the reflected wave is called the reflection method, and the measurement method using the transmitted wave is called the through transmission method.

Acoustic impedance is highest for solids, lower for liquids, and even lower for gases. The acoustic impedance of gases is more than three orders of magnitude lower than that of solids. Due to this large difference in acoustic impedance, delamination areas, and voids reflect nearly 100% of the incident wave, providing a large contrast with the surrounding area in reflection method images, and making defect detection easy. Gaps of 5 nm in the direction of the delamination depth are considered detectable[(1)].

Probe Resolution

A probe is a device that sends and receives ultrasound by using a piezoelectric element to transform electrical signals into mechanical vibrations, or inverse-transform mechanical vibrations into electrical signals. Since high resolution is required for inspecting electrical devices, the probe has an acoustic lens at its tip that is used to transmit a focused beam into the specimen. The beam spot size diameter in water d_{-6} is given by equation (2) below, from the focal distance F, and the acoustic lens aperture diameter D.

$$d_{-6} = \alpha \frac{\lambda F}{D} \quad (2)$$

Here α is a coefficient, and λ is the wavelength of the ultrasound in water. The speed of sound in water v and the frequency of the ultrasound f are expressed by equation (3) below.

$$\lambda = \frac{v}{f} \quad (3)$$

The ultrasound emitted from the probe is not a single frequency. Instead, it has a waveband with a peak at a particular frequency, so f is considered to be this peak frequency.

Equation (2) indicates three methods of improving probe resolution: Reducing the wavelength (i.e., increasing the frequency), reducing the focal distance, and increasing the aperture diameter. However, in practice, two of these methods (reducing the focal distance and increasing the aperture diameter) are sometimes ineffective for nondestructive inspection. When the aperture diameter is increased, refraction will occur according to Snell's law in the course of propagating the ultrasound into the specimen from water. As a result, even if the aperture diameter is increased, only the ultrasound emitted from the center of the lens will actually penetrate into the specimen. Reducing the focal distance is only effective for defects near the surface. Accordingly, frequency is the key to high-resolution/high-definition measurements.

RESOLUTION-ENHANCING TECHNOLOGY

Principles of Resolution-enhancing Technology

As described in the previous chapter, increasing the frequency is the key to enhancing resolution. Hitachi Power Solutions has therefore developed a high resolution (HR) unit that narrows the bandwidth of the frequency components of the ultrasound emitted by the probe and shifts its frequency higher. It can be connected to Hitachi Power Solutions' SATs as an option. Fig. 3 shows a block diagram of when the HR unit is connected. When the HR unit is connected, it is equipped with the standard transmitter along with the HR unit for high-resolution measurement, and is configured to enable either device to be selected from the personal computer (PC) used to set the measurement conditions.

Fig. 4 shows fast Fourier transforms (FFTs) of the reflected wave signal obtained from the same location at the interface between a flip chip/chip scale package (FC/CSP) large-scale integration (LSI) silicon chip and its underfill resin, using a probe with a nominal

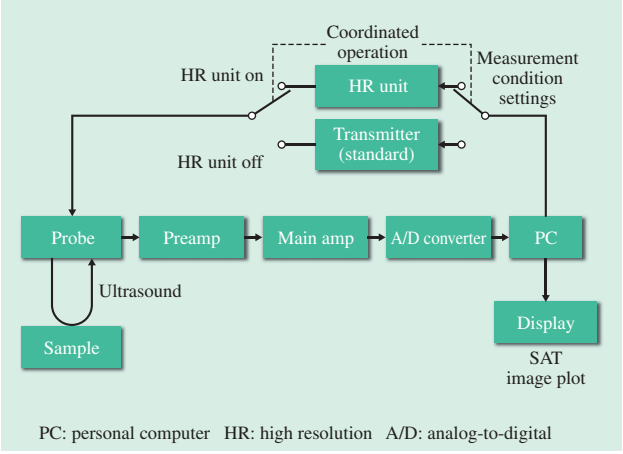

Fig. 3—Block Diagram When Optional HR Unit is Connected. The HR unit has a function that narrows the bandwidth of the frequency components of the ultrasound emitted by the probe and shifts its frequency higher.

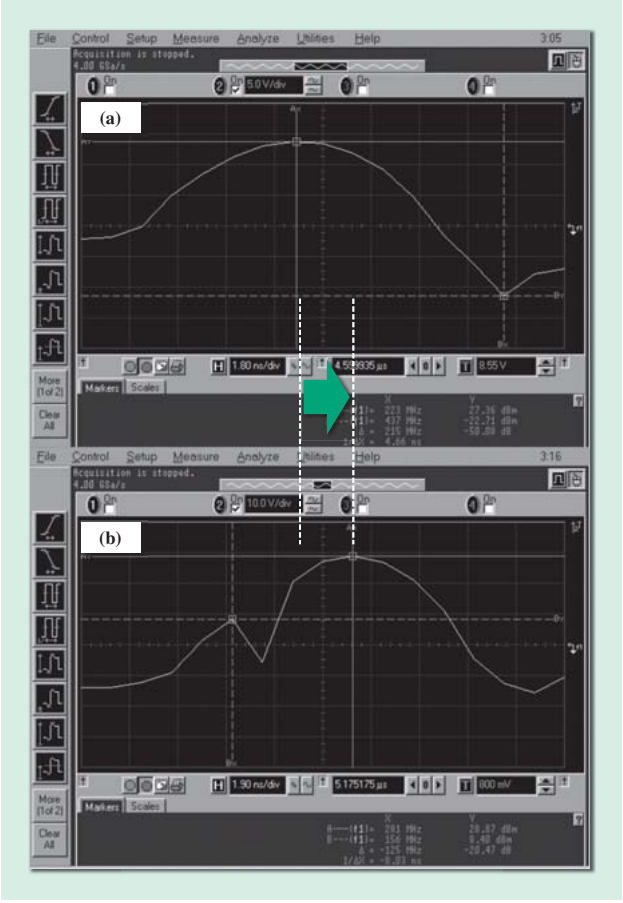

Fig. 4—Narrowing Bandwidth and Increasing Frequency of Transmitted Ultrasound Using the HR Unit.
The graphs above show fast Fourier transforms (FFTs) of the spectrum of the reflected wave signal obtained from the same location at the interface between a flip chip/chip scale package (FC/CSP) LSI silicon chip and its underfill resin, using a probe with a nominal frequency of 250 MHz and a focal distance of 2.9 mm. Graph (a) is the graph obtained when the HR unit is off. Graph (b) is the graph obtained when the HR unit is on.

frequency of 250 MHz and a focal distance of 2.9 mm. When the HR unit is used [Fig. 4 (b)], the peak frequency shifts to 281 MHz, compared to 223 MHz when it is not used [Fig. 4 (a)].

Benefits of Resolution-enhancing Technology

Fig. 5 shows the cross-section of a sample of bonded silicon wafers used to evaluate the HR unit. The sample was created by making grooves 170 nm deep and 1 to 300 µm wide on a silicon wafer, and bonding another silicon wafer on top of the first wafer. Fig. 6 shows the SAT image measured by switching from the standard transmitter to the HR unit during measurement of the bonded silicon wafer sample. The probe used had a nominal frequency of 250 MHz and a focal distance of 1.2 mm, and was focused on the bond interface. The HR unit improved the signal to noise ratio, and improved the contrast between bonded and unbonded parts (indicated by the ellipse in the diagram). As a result, the 2.5 µm and narrower grooves that were almost undetectable without using the HR unit could be detected by using the HR unit (indicated by the circle in the diagram). However, since the 4 µm and narrower grooves were smaller than the ultrasound's beam spot diameter, they all appeared to have the same width.

Fig. 7 shows the SAT image created by observing the interface between the FC/CSP LSI silicon chip and its underfill resin under the conditions of Fig. 4. The image acquired when using the HR unit [Fig. 7 (b)] has detected a more minute defect (indicated by the circle in the diagram) than the image acquired without using the HR unit [Fig. 7 (a)].

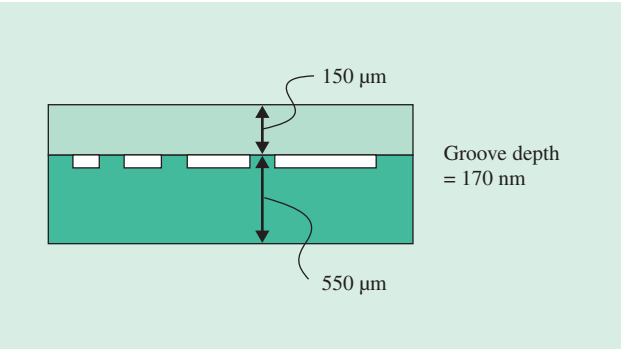

Fig. 5—Cross-sectional Structure of Bonded Silicon Dummy Sample.
The sample was created by making grooves 170 nm deep and 1 to 300 µm wide on a silicon wafer, and then bonding another silicon wafer on top of the first wafer.

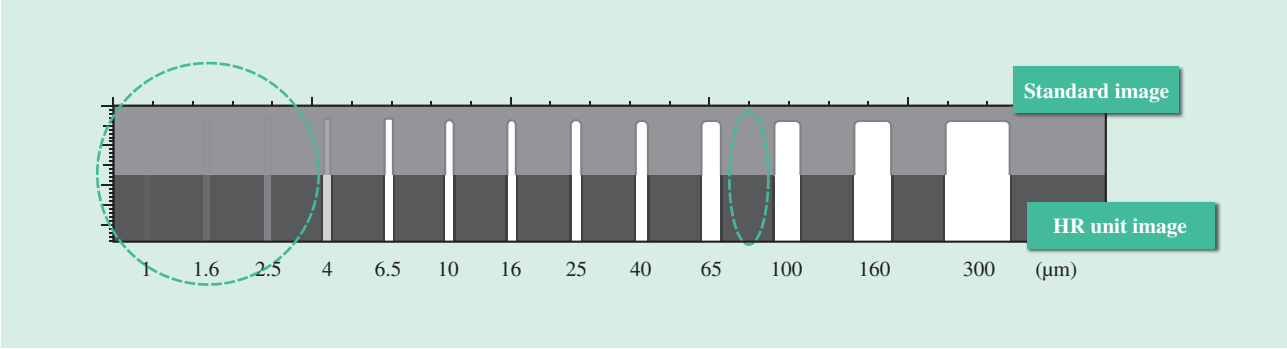

Fig. 6—Improved Detectability Using the HR Unit.
The diagram shows example observations of the bonded silicon sample made using a probe with a nominal frequency of 250 MHz and a focal distance of 1.2 mm. During measurement, the measurement method was switched from the standard method to measurement using the HR unit. The top half shows the standard measurement results. The bottom half shows the results of measurement using the HR unit.

IMAGE RESTORATION TECHNOLOGY

Principles of Image Restoration Technology

High-definition image acquisition is achieved by reducing the beam spot diameter given by equation (2). However, even when the beam spot diameter is reduced, the outlines displayed in SAT images are blurred as a result of the ultrasound intensity distribution in the diameter direction. This blurring results in small defects being missed. To address this problem, Hitachi Power Solutions has developed image restoration technology that is provided as an optional function. It uses image processing to remove blurring from SAT images.

The SAT image $O(x, y)$ can be modeled by the following equation[2]:

$$O(x, y) = G(x, y) \otimes X(x, y) + N(x, y) \quad (4)$$

Here x, y are the coordinates in the image, $X(x, y)$ is the ideal image that should be obtained, $N(x, y)$ is noise, and $\otimes$ is an operator that performs position convolution. $G(x, y)$ is the ultrasonic intensity distribution (the point spread function, PSF) of the beam spot that causes blurring. The beam spot diameter d_{-6} can be calculated from equation (2) using the specifications of the probe used to acquire the image, and $G(x, y)$ can be approximated by the Gaussian distribution given by equation (5) below.

$$G(x, y) = \frac{1}{2\pi d_{-6}^2} exp\left(-\frac{x^2 + y^2}{2d_{-6}^2}\right) \quad (5)$$

The ideal image with blurring removed $X(x, y)$ is obtained by removing the noise $N(x, y)$ from the SAT image $O(x, y)$, and using the PSF to perform deconvolution[3].

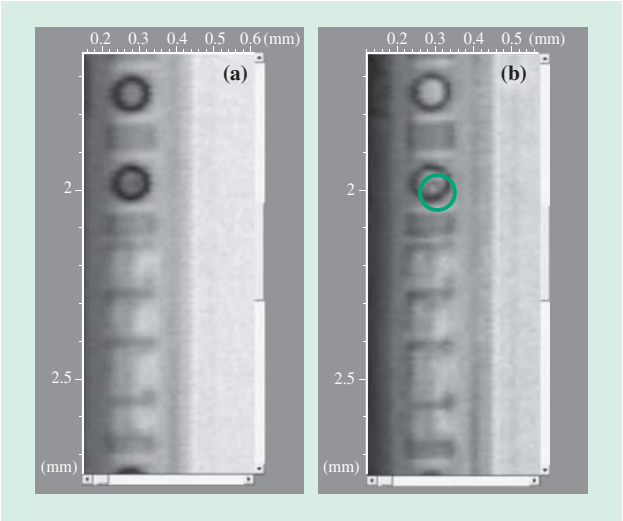

Fig. 7—Improved Detectability on Actual Sample Using the HR Unit.
The images above show the results of example observations of the interface between an FC/CSP LSI silicon chip and its underfill resin, made using a probe with a nominal frequency of 250 MHz and a focal distance of 2.9 mm. Image (a) shows the result of standard measurement. Image (b) shows the result of measurement using the HR unit.

Benefits of Image Restoration Technology

Figs. 8 (a) and 8 (b) show a SAT image, and the restored image created from it, using image restoration technology. The SAT image was created by observing the interface between an FC/CSP LSI silicon chip and its underfill resin, using a probe with a nominal frequency of 200 MHz and a focal distance of 6.9 mm. Figs. 8 (c) and 8 (d) show the signal strength distribution between points A and B in the images of Figs. 8 (a) and 8 (b). The round shapes in the SAT

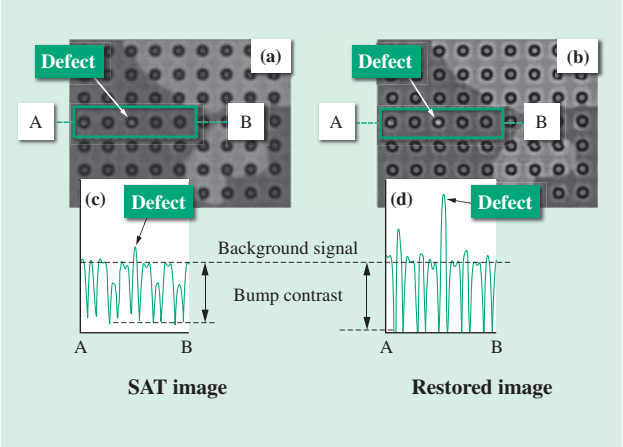

Fig. 8—Using Image Restoration Technology to Reveal Defects. The images above show the results of applying image restoration technology to the result of an observation of the interface between an FC/CSP LSI silicon chip and its underfill resin, made using a probe with a nominal frequency of 200 MHz and a focal distance of 6.9 mm. Image (a) is the SAT image before applying the image restoration technology. Image (b) is the restored image after applying the image restoration technology. Graph (c) shows the signal strength distribution between points A and B in the SAT image before applying the image restoration technology. Graph (d) shows the signal strength distribution between points A and B in the restored image after applying the image restoration technology.

image [Fig. 8 (a)] represent solder bumps. The area displayed as a defect in Fig. 8 (a) appears slightly lighter than the other bumps, representing a cracked bump. As shown in Fig. 8 (c), it has about the same signal strength as the background signal strength, making it difficult to identify as a defect. However, as shown in Fig. 8 (b), it was possible to find a clear bright spot in comparison to the background image in the restored image created using image restoration. The background signal strength shown in Figs. 8 (c) and 8 (d) is the same, however, the signal strength of the defect was found to be 60% higher.

CONCLUSIONS

This article provided an overview of Hitachi Power Solutions' SAT, and discussed the resolution-enhancing technology and image restoration technology it uses. These technologies improve the detectability of defects that were previously difficult to detect with conventional technology.

The electronic devices used as specimens are expected to become smaller, more multilayered, and more complex in the future. Hitachi Power Solutions plans to continue improving their product's hardware and software and developing new technologies to enable increasingly difficult-to-detect defects to be reliably identified.

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Featured Articles

An Inspection and Measurement Technology Platform Leading the Way to More Advanced Manufacturing

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Hiroyuki Nakano, Dr. Eng.
Shin-ichi Taniguchi, Ph.D.
Toshiharu Miwa, Dr. Eng.

OVERVIEW: The inspection and measurement of things is indispensable to manufacturing activities in order to guarantee that products are manufactured as designed. For inspection and measurement in the manufacturing industry, Hitachi's Research & Development Group has set forth an inspection and measurement technology platform consisting of four core technologies: (1) visual inspection and metrology, (2) nondestructive inspection, (3) chemical measurement and probe imaging, and (4) optical 3D shape measurement. The group for the technology platform is working on developing inspection and measurement technologies designed to handle a variety of objectives. By improving the four core technologies, the group will help improve the quality and ensure the reliability of Hitachi's manufacturing activities, and lead the growth of the inspection and measurement equipment business segment. To illustrate some examples of the development of these core technologies, this article describes technologies for visual inspection of semiconductor wafers, nondestructive inspection, using X-rays and supersonic waves, nano-resolution microscopy, bio-molecular measurement, and optical 3D shape measurement.

INTRODUCTION

NEEDLESS to say, the inspection and measurement of things is indispensable to manufacturing activities in order to guarantee that products are manufactured as designed. Although these activities are indispensable for quality assurance, the investment in plant equipment that is required for them tends to be underfunded because they do not contribute directly to production. In practice, outstanding inspection and measurement technologies are necessary for improving plant-wide productivity and quality. In addition to ensuring product quality and reliability, this platform also provides benefits such as reducing defects generated in manufacturing processes, and automating manufacturing processes by eliminating adjustment and setup work. The Internet of Things (IoT) has recently become a focus of media attention. The inspection and measurement technologies used with new manufacturing methods that make use of the IoT are core technologies that measure object states in real time and store them as digital data. Combining real-world data and various simulation technologies in virtual spaces is creating advances in mass customization enabling immediate manufacturing of products that are tailored to a wide variety of client needs.

Designed to help improve quality and ensure reliability for Hitachi manufacturing and to lead the growth of the inspection and measurement equipment business segment, the Hitachi, Ltd. Research & Development Group's inspection and measurement technology platform for the manufacturing industry sets forth four core technologies: (1) visual inspection and metrology, (2) nondestructive inspection, (3) chemical measurement and probe imaging, and (4) optical three-dimensional (3D) shape measurement. The group for the technology platform is seeking to augment technology development in these core areas, which cover a wide array of product segments ranging from mechanical parts to materials and process products. It is working on developing high-precision external and internal defect detection technologies and advanced technologies to enable imaging and visualization of previously unseen states and phenomena.

This article describes the characteristic strengths of these core technologies, their use in Hitachi's manufacturing, and their application to inspection and measurement equipment.

VISUAL INSPECTION AND METROLOGY

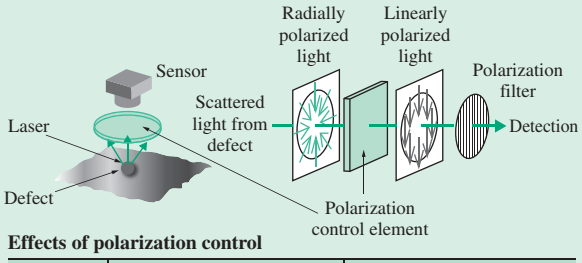
Hitachi is developing visual inspection and metrology tools based on optical detection technology and image processing technology for detecting minute particles and defects in products.

Semiconductor Wafer Inspection

World-class inspection technologies are developed that enable high-speed, and highly-sensitive detection of defects on semiconductor wafers. The developed technologies are applied to Hitachi High-Technologies Corporation's visual inspection tool. They enable nanometer-scale defect control, helping improve the manufacturing yields and product reliability of device manufacturers.

Optical Detection Technology

A highly-sensitive optical defect detection system has been realized with a polarization control element that was developed using simulation with both a scattered light model of defects by laser emissions and vector beam propagation analysis[1]. The polarization control element converts radially polarized scattered light from a defect to linearly polarized light. And a polarizing filter selectively filters out scattered light from the wafer surface so as to enable stable detection of 18-nm size defects (see Fig. 1).



Effects of polarization control

Polarization control	X/Y polarization intensity on sensor		Detected light intensity on sensor	
Off	X polarization	Y polarization		
On	X polarization	Y polarization		

Fig. 1—Optical Defect Detection System.
Scattered light from defects (radially polarized light) is detected by converting it to linearly polarized light, increasing its discrimination factor relative to scattered light from the wafer surface, and enabling high-sensitivity detection.

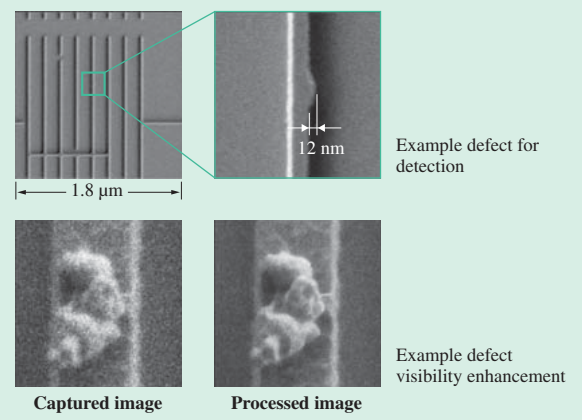


Fig. 2—Image Processing for Defect Inspection.
Hitachi is developing image processing algorithms for minute defect detection/visibility enhancement.

Image Processing Technology

As semiconductor process design rules continue to shrink, the size of a defect becomes as much as the pattern variation derived from production tolerance. To solve this issue, advanced defect-detection algorithms are needed. Hitachi is working on creating more sensitive detection algorithms by combining conventional gray-scale-based image comparison methods with more advanced perturbation matching[2] and feature-based pixel comparison methods.

Scanning electron microscope (SEM) images are helpful for detailed defect observation. For improving defect visibility, Hitachi has developed image enhancement algorithms[3] including a noise reduction and image resolution enhancement based on an optical system detection model (see Fig. 2).

NONDESTRUCTIVE INSPECTION

Hitachi is developing non-destructive inspection technologies for visualizing the inside of a product using X-rays and supersonic waves. The developed technologies are used in Hitachi's industrial high-energy X-ray computed tomography (CT) scanners, and in Hitachi Power Solutions Co., Ltd.'s ES Series of ultrasonic testing systems. They contribute to efficiency, and improvement of manufacturing process and product quality.

Industrial High-energy X-ray CT

The conventional (second-generation) method required translation and rotation operations for one cross-sectional image. To enable rapid imaging without decreasing the detection accuracy, Hitachi

has developed a new (third-generation) method that can create an image using only rotation operations, by densely arranging thin semiconductor sensors as detecting elements. The new method achieves high-speed imaging at a maximum speed of ten seconds per cross-section[4].

A detector array with between 500 and 1,000 elements per row is placed in opposition to an X-ray source. Using a collimator that is aligned with a high degree of accuracy, only the X-rays from the specific direction are incident on each element, thereby preventing cross-talk between elements and enabling both high-speed imaging and highly accurate detection (see Fig. 3).

Ultrasonic Inspection Technology

Hitachi developed inspection technology that uses two ultrasonic waves with orthogonal vibration axes[5]. In the conventional method, it was difficult to identify defect signals because of reflection noise generated at the crystal interface, and only defects of the order of several millimeters could be detected. Using two ultrasonic elements that send and receive ultrasonic waves having orthogonal vibration axes, it is now possible to acquire the signal of each axis individually. For example, in rolled steel, two ultrasonic waves having orthogonal vibration axes have different propagation speeds. So, the defect signal of each wave appears in a different position. Based on the difference in propagation speed, a method to correct the defect signal position was developed. As a result, the signal-to-noise ratio (S/N) improved, and defect detection on the order of sub-millimeters was achieved (see Fig. 4). In future, this method will be commercialized for use in the receiving inspection of procurement materials.

CHEMICAL MEASUREMENT AND PROBE IMAGING

Hitachi's research centers are leading the way in the development of technologies for detecting high-resolution optical images that could not be seen previously, and for measuring molecular functions. The goals of these technologies are applications such as quality control for cutting-edge devices, and medical diagnoses using disease-linked bio-molecules.

Nano-resolution Microscope

Hitachi is developing a probe-type microscope that enables nano-resolution measurement of physical properties and composition states. It is designed for applications such as quality assurance of cutting-edge devices and inline inspection during manufacture. A nano-sized spot of light is generated at the tip of

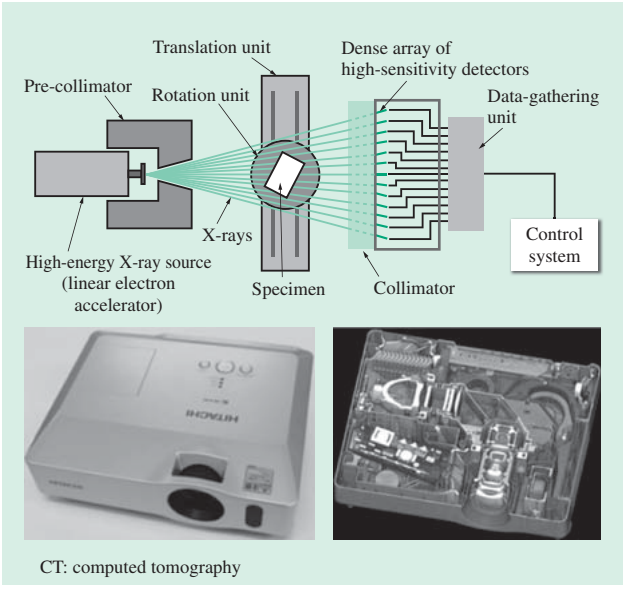


Fig. 3—Industrial High-energy X-ray CT Scanner Configuration and Internal Imaging Result.
The top diagram shows the configuration of an industrial high-energy X-ray CT scanner. The bottom-right image is the internal imaging result. The scanner achieves a 0.2-mm resolution using a dense array of high-sensitivity detectors and a collimator.

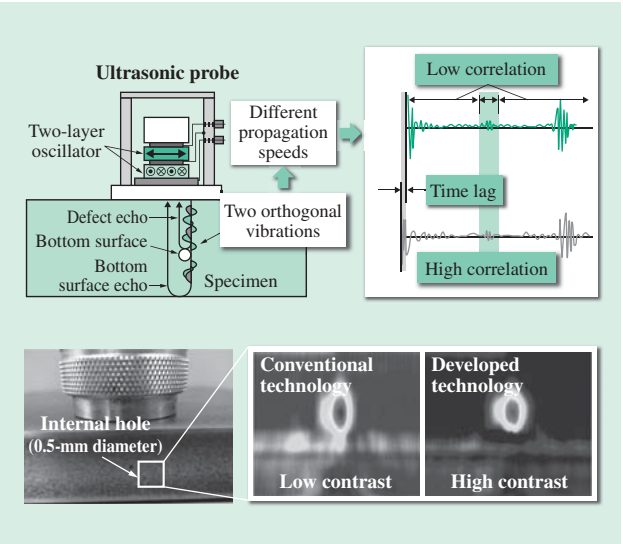


Fig. 4—Two-axis Ultrasonic Probe Configuration/Detection Waveform and Internal Imaging Result.
The top diagrams show the configuration and detected waveforms of a two-axis ultrasonic probe. The bottom-right images are the internal imaging results. Using the correlation between ultrasonic waves having two axes, the equipment can detect sub-millimeter-sized defects.

the probe, and scanned to enable the acquisition of a nano-resolution optical image that greatly exceeds the diffraction limit.

Fig. 5 is a schematic diagram of the developed detection probe. A plasmon waveguide composed of a gold film formed on a silicon cantilever tip converts incident light to surface plasmons that are efficiently coupled with a carbon nanotube (CNT) optical probe. As a result, near-field light of about 4 nm in diameter is generated at the CNT optical probe tip, and is used to enable imaging of a nano-resolution optical image on a sample. In addition to applications for characteristic analysis of devices and materials, this technology will ultimately lead to the development of nondestructive measurement tools for cells.

Bio-molecule Capture/High-sensitivity Measurement Using Molecularly Imprinted Polymers

Hitachi has developed molecularly imprinted polymer technology that enables advanced medical diagnosis through the measurement of disease-linked bio-molecules existing in trace concentrations (nmol/L) in biological samples[6), 7)]. Molecularly imprinted polymer technology uses a target molecule as a template to create a polymer nearby. The surface of the polymer has holes shaped like the target molecule. By covering the surface of a core particle (made of polystyrene) with the molecular template polymer, the aim is to efficiently capture trace molecules to achieve high-sensitivity measurement (see Fig. 6).

OPTICAL 3D SHAPE MEASUREMENT

For high-efficiency production and the quality assurance of products, it is important to measure shapes during manufacture and to provide measurement results as feedback for the design, processing, and assembly processes. Hitachi is therefore working on developing laser-driven high-precision 3D shape measurement technology.

Hitachi has developed technology that enables contact-free, high-precision shape measurement using lasers, such as optical comb lasers with comb spectrum characteristics, as well as technology for processing/analyzing measured large-volume 3D point cloud data[8), 9)]. It is working on developing technologies to support parts ranging from large machinery parts in equipment such as generators, compressors, and railway car bodies, to small parts with complex shapes such as automotive parts (see Fig. 7).

CONCLUSIONS

In addition to the technologies described in this article, the inspection and measurement technology platform also encompasses work on developing inspection and measurement technologies for various other objectives

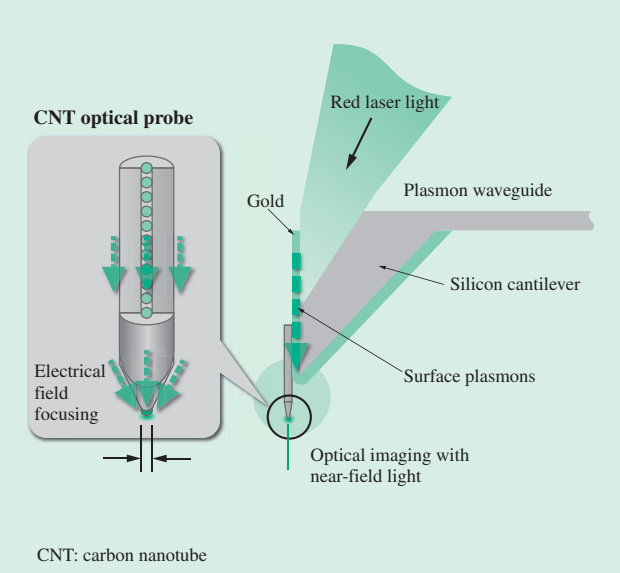


Fig. 5—Schematic Diagram of Developed Optical CNT Probe.
A plasmon waveguide generates near-field light at the tip of a gold-coated silicon cantilever. The light is scanned to enable acquisition of a nano-resolution optical image.

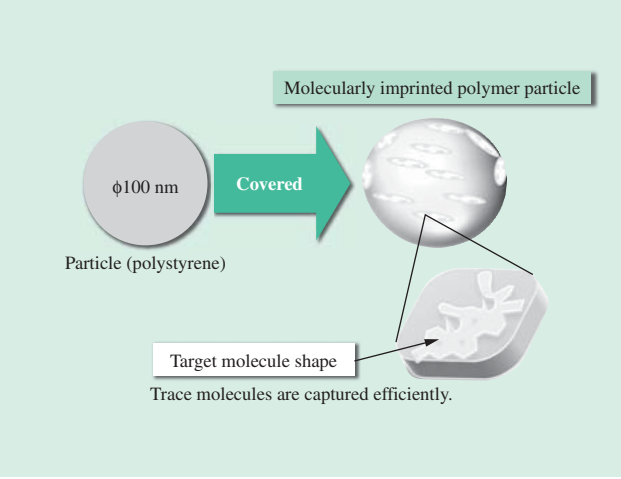
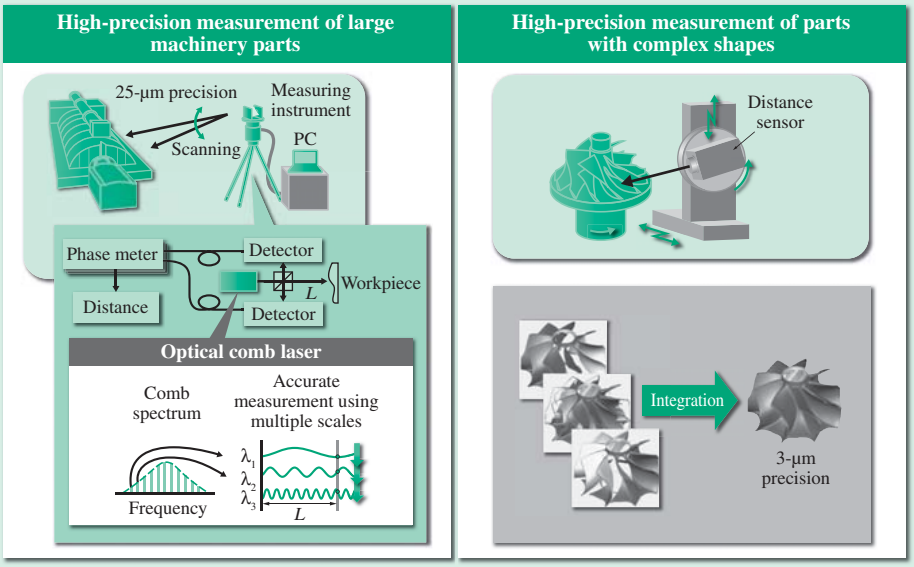


Fig. 6—Schematic Diagram of Molecularly Imprinted Polymer Particle Creation.
The surface of a polystyrene particle is covered with a molecularly imprinted polymer corresponding to the target molecule. This enables the high-sensitivity measurement of trace molecules by forming holes that efficiently capture the target molecule.



PC: personal computer 3D: three-dimensional

Fig. 7—High-precision 3D Measurement Technology. Hitachi has developed technology for contact-free, high-precision measurement of shapes ranging from large machinery parts in equipment such as generators and compressors, to small parts with complex shapes such as automotive parts.

and methods. This work will assist the inspection and measurement activities of Hitachi's manufacturing, and lead the growth of Hitachi's inspection and measurement equipment business segment.

Moreover, advances in IoT-based manufacturing will result in increasing use of digital data enabled by advanced inspection and measurement technologies, continuing to help make Hitachi manufacturing more advanced.

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Topics

Global Collaboration with CEMES, French National Center for Scientific Research

—Joint Project to Implement Aberration Corrector in High-end TEM—

INTRODUCTION

IN collaboration with the Center for Materials Elaboration and Structural Studies (CEMES), an institute of the French National Center for Scientific Research (CNRS), Hitachi High-Technologies Corporation has developed a high-end field emission-transmission electron microscope (FE-TEM) that incorporates a spherical aberration corrector. Delivered to CEMES in 2012, the instrument boasts the highest resolution in the world (spatial resolution of 0.5 nm in magnetic-field-free locations)*1.

This article looks back at the events that led to the success of this collaboration.

REQUEST FROM CEMES

CEMES is a research institute attached to CNRS, and is known as one of Europe's leading materials research centers. CEMES is also renowned for its high level of electron microscope technology, and developed a proprietary ultra-high voltage electron microscope in 1958. It has recently developed a microscopy technique known as dark-field electron holography.

Around 2007, CEMES began a project to develop and install a new electron microscope designed to assist with the research and development of next-generation semiconductors. To provide support for strained silicon*2 (a material that enhances semiconductor device performance), one of the project objectives was to develop technology and applications for electron holography-based observation and measurement of strain distributions within devices.

CEMES requested that Hitachi High-Technologies partner with them in the project. This was because Hitachi High-Technologies' cold-field emission (FE) electron gun (cold cathode field emission electron gun) technology can produce highly coherent electron beams of high brightness and high-energy resolution, making it well suited to electron holography.

RESPONDING TO THE CEMES RESEARCHERS' PASSION

Hitachi High-Technologies had previously released a high-end transmission electron microscope (TEM), model HF-3300(1), an FE-TEM containing a cold FE electron gun.

CEMES wanted Hitachi High-Technologies to mount a spherical aberration corrector developed by Prof. Dr. Max Haider of the German manufacturer Corrected Electron Optical Systems GmbH (CEOS) in the HF-3300, however, there were many barriers to achieving this goal. Hitachi High-Technologies had previously partnered with CEOS to develop a scanning transmission electron microscope (STEM) containing a spherical aberration corrector (model HD-2700). However, with this request, CEMES wanted Hitachi High-Technologies to modify one of its existing products by mounting another company's device on it, and Hitachi High-Technologies' quality control standards dictated that performance could not be guaranteed after such a modification. Moreover, since the CEMES project would be handled as a custom order, there were that concerns it would affect the plant's production schedule and other products, and many in the company were against taking part in the project.

Ultimately, it was the enthusiasm of the CEMES researchers and the passion of Hitachi High-Technologies' marketing and design people to respond to that enthusiasm that overcame these obstacles.

The project represented Hitachi High-Technologies' first delivery to CEMES, although CEMES already had two Hitachi High-Technologies HF-2000 FE-TEMs. These HF-2000 microscopes had been obtained by project member Dr. Florent Houdellier in 2005 from universities in the UK and Switzerland. After being personally dismantled, transported, reassembled,

*1 Electron microscopes use a magnetic field in their electron lens, so the sample is usually affected by the field. Applications such as observing the magnetic domains of magnetic materials require the sample to be unaffected by the magnetic field, a state known as *magnetic-field-free*.

*2 A technology that improves the performance of semiconductor devices by straining the silicon crystal lattice to enhance electron/hole mobility. Measuring and controlling the strain on the silicon crystal lattice are important for semiconductor manufacturing process control.

and adjusted by Dr. Houdellier, the TEMs had been in use for various types of testing and research at CEMES. This hands-on experience with Hitachi High-Technologies' electron microscopes gave CEMES researchers thorough knowledge of their advanced core technologies, making CEMES eager to have the company take part in the project. Inspired by the spirit of discovery and the enthusiasm of Dr. Houdellier and the other CEMES researchers, Hitachi High-Technologies' marketing and design divisions became passionate about living up to their expectations.

The problematic issue of guaranteeing performance was resolved by meticulously defining each area of responsibility over a series of meetings among CEMES, Hitachi High-Technologies, and others involved with the project. It was determined that maximizing the aberration correction performance would require improvements to the electron microscope's mechanical and electrical stability, and the aberration corrector would be mounted on the HF-3300S after these improvements had been achieved. A solid relationship of mutual trust was gradually built up, with Hitachi High-Technologies' design division working hard on solving problems through uncompromising and frank back-and-forth discussions with CEMES about the technology. To respond to concerns about the effect of the project on Hitachi High-Technologies' production schedule, the advantages and expected benefits of partnering with CEMES were presented within the company, and participation in the project was eventually approved through support from related organizations. CEMES and Hitachi High-Technologies signed an official agreement in January 2011.

However, two months later, Hitachi High-Technologies' production center in the Naka Division of Ibaraki prefecture suffered major damage from the Great East Japan Earthquake. It was forced to close for about a month, and the scheduled delivery date was scrapped. A sales representative posted to Hitachi High-Technologies Europe GmbH immediately visited CEMES to apologize for the delivery delay. He made an effort to determine exactly when and how the plant would be repaired and ready for operation again, and to faithfully report the findings to CEMES. Eventually these challenges were overcome, and a new delivery plan was submitted, leading to the project's completion with the September 2012 installation and handover of the equipment.

The custom FE-TEM delivered to CEMES is both a holography electron microscope, enabling interference fringe observation, and a Lorentz microscope[*3], enabling kinetic in situ observation of changes to materials at the atomic level. It was therefore named I2TEM, in reference to the two initial i's of *interference* and *in situ* (see Fig. 1).

I2TEM WORKSHOP

In June 2013, CEMES held a two-day event consisting of an I2TEM completion ceremony and a workshop. The event served as an opportunity to showcase the anticipated results from I2TEM. Researchers presented data obtained after the equipment's delivery, such as semiconductor strain distributions observed using dark-field electron holography, and magnetic field distributions in magnetic nanowire.

The event was attended by about 100 researchers and others from CEMES, CNRS, and other organizations in Europe. It was also attended by researchers from Hitachi's Central Research Laboratory in Japan. Congratulatory remarks were delivered by the Director of the CNRS Institute of Physics, an acting mayor, a provincial governor, and the heads of scientific research divisions. The event was covered by the French newspaper *Le Monde*, which reported that I2TEM was the result of a collaboration between CEMES and Hitachi High-Technologies.

*3 An electron microscope configured so that the position of the sample prevents it from being affected by the magnetic field of the objective lens. Used for applications such as observing the magnetic domains of magnetic materials.

CEMES: Center for Materials Elaboration and Structural Studies
CEOS: Corrected Electron Optical Systems GmbH
TEM: transmission electron microscope

Fig. 1—I2TEM, Developed and Delivered in Collaboration with CEMES.
I2TEM was created by mounting a CEOS aberration corrector in Hitachi High-Technologies' HF-3300S TEM. I2TEM can perform both interference fringe observation and atomic-level kinetic observation (in situ observation), and so it was named I2TEM in reference to the two initial i's of interference and in situ. An inscription reading '愛²TEM' (愛 is pronounced 'I' and means 'love') was added to the main body to commemorate the passion of the project participants.

A signing ceremony for the partnership agreement between CEMES and Hitachi High-Technologies took place in the presence of the CNRS chief executives in September 2014. The agreement officially outlines how CEMES and Hitachi High-Technologies will collaborate on electron microscope R&D.

I2TEM APPLICATIONS

CEMES foresees I2TEM being used for measuring the magnetic fields of the permanent magnets that drive high-performance hybrid and electric vehicle motors. I2TEM can make high-resolution observations of magnetic materials in a magnetic-field-free state (a state in which the materials are unaffected by the field). CEMES is planning to take advantage of this feature to measure the boundary magnetic forces of rare earth materials, and apply the results to explicating magnetic force mechanisms and to materials research.

Another I2TEM use anticipated by CEMES is in measuring the magnetic fields of the magnetic heads used in hard disk drives (HDDs), to help increase HDD density and read/write speed. The organization is also looking into the use of I2TEM for cancer treatments and other medical applications, and anticipates its use in the development of new materials and in pioneering new industrial and academic areas.

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Topics

TM Series Tabletop Microscopes: Creating a New Market, Initiatives for Social Responsibility

—Advancing Electron Microscopes with Improved Usability and Accessibility—

INTRODUCTION

RELEASED in 2005, the TM series of tabletop electron microscopes manufactured and marketed by Hitachi High-Technologies Corporation are designed to combine the resolution of an electron microscope with the ease-of-use of an optical microscope. Since the TM series models have few installation environment restrictions and are easy to handle they are in widespread use among new electron microscope users such as private-sector companies, universities, government offices, and science museums. Sales have exceeded 3,300 units (as of January 2016).

With their compact size and simple operation, the TM series models are being brought to various events and sites such as science museums, elementary schools, and junior high schools, giving children the chance to experience the micro-world. Seeing the micro-world for the first time gives children the chance to become interested in science, helping foster the next generation of scientists who will further the advance of science and technology in the future.

This article describes the development concept of the TM series, how the series is creating a new market, and how the Hitachi High-Tech Group is using the series in its corporate social responsibility (CSR)activities.

TM SERIES DEVELOPMENT CONCEPT

The development concept of the TM series was to create a series of cutting-edge microscopes enabling easier operation and greater accessibility. The series went on sale in April 2005 (see Fig. 1).

Electron microscopes have come into widespread use, being used as a tool for applications such as research and development (R&D) and product quality control in various fields. However, restrictions on electron microscope installation environments previously made it impossible to install them in school science labs or corporate offices. Samples also had to be placed in a vacuum, requiring sample preprocessing that demanded time and experience.

However, around 1991, Hitachi High-Technologies added a variable pressure scanning electron microscope (SEM) to its SEM lineup. This SEM model enabled observations with a sample chamber pressure ranging from a few pascals to about 260 pascals, enabling observation of samples containing moisture or oil and dramatically increasing the number of SEM users. Inspired to give more people the chance to experience the micro-world, Hitachi High-Technologies started developing SEM models with simple, easy operation. Eventually the company developed the TM series, a lineup of tabletop electron microscopes that can be easily installed even in school classrooms. TM series models can be operated just by connecting them to a standard 3-socket 100-volt alternating current (AC) wall outlet, and eliminate the need for time-consuming sample preprocessing. They also provide a carefully selected lineup of functions for observation, resulting in most operations being automated. These features let even first-time users operate TM series models as easily as a digital camera, enabling operation by children and adults alike regardless of experience.

Fig. 1—TM3030Plus Tabletop Microscope.
The TM3030Plus is a tabletop-sized electron microscope, giving it few restrictions on installation locations.

HOW THE TM SERIES IS CREATING A NEW MARKET

When first released, the TM series models were simply instruments for observing enlarged images of sample surfaces. But as sales increased, users began asking for features such as the ability to observe samples being cooled, or to analyze sample compositions. To meet these needs, optional features were added such as a cool stage enabling sample cooling and an X-ray analysis unit. The ease-of-use of the TM series resulted in increasing use for quality control on manufacturing sites that had previously used visual inspection or optical microscopes for this purpose. And, with its easy operation and lack of installation environment restrictions, the TM series is being used by elementary schools, junior high schools, and other educational institutions, as well as facilities such as natural history museums, science museums, and theme parks.

Since TM series models are compact and lightweight (model TM3030 weighs about 63 kg), they can easily be brought to a variety of event sites. Naturally, they can be brought to elementary schools or junior high schools, and they are being used in science guest lectures provided through CSR activities by various groups. These initiatives are letting a greater number of people experience the micro-world through electron microscopes.

The next chapter discusses how Hitachi High-Technologies is using the TM series in its CSR activities.

USING THE TM SERIES IN INITIATIVES SUPPORTING CSR ACTIVITIES

To support the activities of organizations that actively plan and organize original educational programs designed to familiarize children with science, the Hitachi High-Tech Group has been lending TM series models since the series was first released. To give preschoolers and students opportunities to experience the micro-world, the Group has recently been actively participating in several events organized by science and technology institutes, such as the Hitachi Science Seminar on Electron Microscopy, and the Concours of Schoolchildren's Inventions, along with the Nippon Cultural Broadcasting radio program Masaki Omura's Science Kids. Hitachi employees are also engaging in CSR activities tied to local communities by visiting elementary schools and junior high schools to provide guest lectures using TM series models (see Fig. 2).

These activities are not limited to Japan, and are also being actively implemented in the USA. Hitachi High Technologies America, Inc. (HTA) is helping promote the STEM field education being advanced by President Obama (STEM stands for science, technology, engineering, and mathematics). STEM field education is being emphasized as a way to train the human resources needed by science and technologies fields, and the key to making the USA stronger as a nation. HTA is an active participant in events organized by schools and science museums, routinely bringing the TM series to sites to give visitors hands-on experience of the micro-world and the equipment. From September 2011 to December

Fig. 2—Science Museum Electron Microscope Event. Hitachi High-Tech Group provided assistance for an exhibition held at the Hamagin Space Science Center that introduced children to the micro-world by demonstrating how microscopes magnify small objects.

2015, HTA took part in over 500 educational support activities throughout the USA.

The Hitachi High-Tech Group will continue to use the TM series in educational support activities throughout the world, helping the advancement of science and technology.

CONCLUSIONS

This article has described the development concept of the TM series, how it is creating a new market, and how the Hitachi High-Tech Group is using it in its CSR activities.

The Hitachi High-Tech Group will continue to provide opportunities to experience the micro-world, letting more children become inspired by the wonders of science, and helping instill an interest in science and technology. It will continue to meet the responsibilities we have as a corporate citizen by making ongoing contributions that draw on the business characteristics of the Hitachi High-Tech Group.

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