Thirty years of sample preparation: Where we have been and where can we go?

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INTRODUCTION

Congratulations to the staff of *Microscopy and Analysis* on the journal's 30th anniversary. Since its onset, *M&A* has striven to present pertinent information to the global microscopy community in a highly professional manner. We must acknowledge the founder, Jean Gordon, for articulating the vision and having the persistence and tenacity to create an enduring publication that has raised the bar of microscopy communications.

There have been substantive changes in the microscopy field over the past 30 years; microscope technology has evolved, the tools and techniques for sample preparation have become more sophisticated, and the material range and depth of characterization have expanded.

THE EVOLUTION OF THE ELECTRON MICROSCOPE

Since the birth of *M&A*, the electron microscope itself has evolved in terms of its performance and capabilities. This corresponds to both image resolution and analytical data.

A significant improvement in electron optics occurred in the early 1990s with the commercial deployment of field emission gun (FEG) technology. FEG sources generated an electron beam sufficient to yield resolution approaching 1 Ångström.

In the early 2000s, advances in microscope goniometer and specimen holder technology allowed specimens to be tilted to high angles and imaged in precise increments. The compilation of the corresponding images permitted the reconstruction of this data into a three-dimensional (3D) format – tomographic reconstruction. Imaging of features contained within the specimen that are not always visible in a two-dimensional projection became obvious in 3D. Because of the increase in information provided by 3D tomography, it is now a mainstream technique.

Another major TEM milestone was the commercialization of the aberration-corrected TEM in 2005. The key to aberration-corrected technology is having an electron probe size that approaches its theoretical limit based upon the wavelength of electrons. An electron probe that is smaller than the spacing between atoms yields both structure and chemistry at the atomic level. At the time of its introduction, the future of microscopy was at an inflection point. There were questions relative to the significance of such a technological breakthrough, as well as the total global market of aberration-corrected microscopes. Not foreseeing the significance of this technology, some forecasted a demand of 10 instruments. Today, there are more than 500 aberration-corrected TEMs around the world and the impact on science has been significant.

During the past 30 years, many of the technological advantages associated with TEM have also been applicable to scanning electron microscopes (SEM), with resolution significantly improving over time. But more notably, the improved resolution is achieved at low accelerating voltages (< 2 keV), which means that there is much less interaction between the electron beam and the specimen. As a result, the quality of the top few nanometers of material has become more important, which in turn has led to a demand for higher quality specimen preparation tools and techniques.

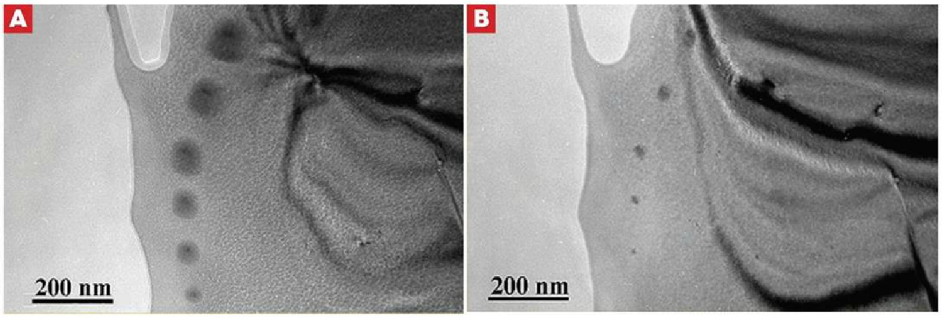


FIGURE 1 Removal of existing carbonaceous contamination by plasma cleaning. Left, series of six contamination spots following one minute of plasma cleaning. Right, the same six contamination spots following five minutes of plasma cleaning. Note the significant reduction in the size of contamination spots (and the complete removal of the last spot in the series)

FIGURE 2 A conventionally prepared LaTiO3/SrTiO3 TEM specimen. The specimen was wedge polished and then ion milled at a low angle with liquid nitrogen cooling. Annular dark field imaging was done in a FEG TEM

SPECIMEN PREPARATION EVOLVES IN TANDEM WITH MICROSCOPY

Throughout the history of electron microscopy, the ability to prepare samples that exploit the capabilities of the microscope has been a consistent requirement. With each advancement in microscope performance, sample preparation technology had to improve at the same pace.

For materials science applications in the 1980s, a sizable portion of research was related to metals. The trend was beginning to turn, however, toward materials of greater complexity, such as ceramics, oxides, composites, and semiconductors.

Beginning in the 1960s, metals were prepared by jet polishing. With this technique, the electro-chemical reaction between the electrolyte (typically an acid) and the metal thins the central area of the sample to perforation. The area surrounding the perforation is thinned to the point that it becomes transparent to the electron beam.

However, the advent of more advanced materials, particularly those that were not electrically conductive, precludes the use of electropolishing. Thus, the conventional form of specimen preparation was developed and involved the combination of mechanical grinding and ion milling.

At the onset of argon ion milling in the 1970s, ion source technology largely involved hollow-anode discharge, Penning, saddle field, and other types of ion sources without filaments – all of which produced ion beam diameters of a few millimeters and had sufficient current density to allow the thinning of physical science samples within a reasonable amount of time. These ion sources operated at relatively high voltages (3 to 6 kV) and achieved rapid milling rates, but also created a fair amount of sample damage.

Therefore, it became customary to thin the sample as much as possible by mechanical methods to minimize ion milling time. Tripod and wedge polishing, as well as dimpling, became the preferred means to mechanically thin the specimen. However, mechanical thinning also created significant surface damage that needed to be removed by ion milling. Thus, there was a bit of art in striking the right balance of parameters to achieve optimal results.

In the mid-1990s, the focused ion beam (FIB) began its journey to become a powerful method for specimen preparation. The key to the tool's success is its ability to achieve site specificity by allowing the extraction of a specific area of interest, whether it is a grain boundary, an interface between two materials, or an individual device within a semiconductor integrated circuit.

For each major technological improvement to microscopes, the interaction of the electron beam with the specimen became more important – independent of the material being analyzed.

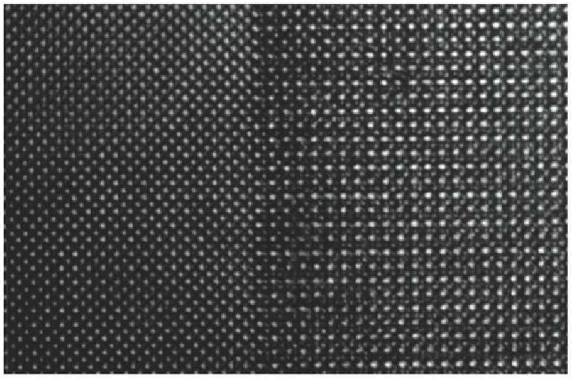
The high current density electron probe associated with FEG technology caused organic contamination on the specimen to polymerize at the impingement point of the electron beam and the specimen, which compromised both the image and the analytical results. This led directly to the development in 1995 of plasma cleaning technology to remove organic contamination from specimens and specimen holders before they are introduced into the microscope column.

For effective plasma cleaning, a low-energy, reactive gas plasma, usually involving some percentage of oxygen, chemically reduces the contamination without altering the properties of the base material. Under ideal conditions, such as when using inductively coupled plasma to produce ion energies less than the sputter threshold of given materials (<15 eV), contamination spots created during previous analyses can also be removed (Figure 1).

Another variable of the interaction of the electron beam and the specimen is specimen thickness, which has progressively decreased through the years. At the onset of FEG technology, specimen thicknesses of ~100 nm were commonplace.

When scanning transmission electron microscopy (STEM) became a mainstream technique in the 1990s, specimen thicknesses needed to be approximately 40 nm to promote suitable scattering effects. The same held true for tomography, which requires thinner specimens because the

FIGURE 3 Ion milling preparation reveals the strontium titanate and strontium ruthenate interface



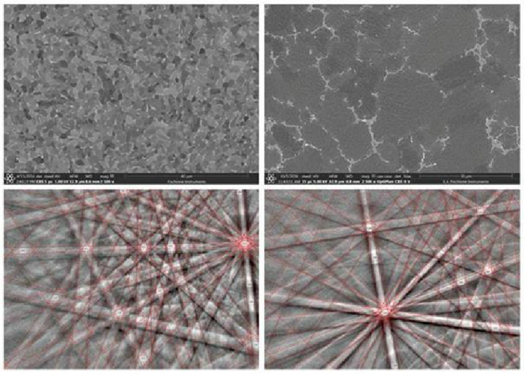


FIGURE 4 Metal alloys prepared by broad beam argon ion milling for electron backscatter diffraction (EBSD) analysis. The first row shows backscatter electron contrast images post ion milling of three metal alloys (zirconium, left; magnesium, center; and titanium, right). The second row shows EBSD patterns of the same alloys

electron beam interacts with a larger material volume as the specimen is tilted to higher angles.

To take advantage of the outstanding capabilities of TEMs with aberration-corrected technology, one must produce artifact-free specimens of ~10 nm in thickness that are as close to atomically flat as possible. It is a challenge to produce specimens of that quality. The typical approach is to extract the specimen from the bulk and thin it to electron transparency. Mechanical or ion beam induced damage, amorphous damage, implanted layers, and organic contamination, all of which can compromise both imaging and analysis, should be avoided, and if they cannot be avoided, they must be minimized before imaging. When one considers that many advanced materials are comprised of various elements with differing properties that thin at dissimilar rates during ion milling, the challenge is then compounded.

A currently accepted workflow for producing the highest-quality TEM specimens is the combination of FIB, followed by low-energy, inert gas, small-spot ion beam technology. Historically, low energy (< 500 eV) has shown significant merit in avoiding damage. Inert gas avoids the possibility of a chemical reaction with the specimen, which is typically the case when using a liquid metal ion source such as gallium (Ga). Small-spot (< 1 µm) technology is the final critical component, because the ions contact only the area of interest. The ability to precisely target the area of interest avoids ion beam contact with the specimen support structure, which can lead to redeposition of the support material onto the specimen. Taking the technology to the next level has involved incorporating an electron column and various detectors (STEM and backscatter) to predict end point by monitoring contrast changes as the specimen thins. This technique has proven to be quite effective in consistently achieving ~10 nm thick specimens that remain representative of the bulk material (Figure 3).

As microscope technology continues to evolve, so will the tools that speed the preparation process without compromising the results. When considering the total workflow, the drive is toward faster time to data, which necessitates enhanced integration of microscopes and specimen preparation tools.

Many traditional TEM specimen preparation techniques are applicable to SEM. As resolution has increased at lower accelerating voltages, greater emphasis is placed on the quality of the surface; therefore, it is important to have the top few nanometers be pristine and representative of the material in the bulk state. This pertains to traditional SEM imaging and analytical techniques, as well as more advanced forms of surface analysis, such as electron backscattered diffraction (EBSD) and electron channeling contrast imaging (ECCI).

For SEM specimen preparation, traditional mechanical grinding and polishing can improve the sample surface, but the improvement is limited by the mechanical damage that is inflicted by the abrasives used in the grinding and polishing process. Broad-beam ion milling, with its ability to polish areas approaching 2 cm, removes mechanically induced damage and yields acceptable surface characteristics for subsequent imaging and analysis (Figure 4).

HOW THIN CAN YOU GO?

The future presents both challenges and opportunities for specimen preparation. In the constant drive to make thinner TEM specimens, we have reached the point where we are trying to reduce specimen thickness from 50 nm to < 10 nm.

At these dimensions, the degree of surface damage becomes critical because the surface now constitutes a greater percentage of the overall sample volume and its corresponding information obtained from the specimen during imaging and analysis. It is equally important to avoid implanted layers, particularly those containing reactive elements such as Ga, which alter the chemistry of the specimen material. Achieving consistency relative to both specimen thickness and quality is a challenge, especially for high-volume applications.

Another microscope technique that requires thinner, less damaged specimens is low-dose TEM, which is used for materials that are beam-sensitive, such as biological substances and polymers. Low-dose TEM also has a role in the imaging and analysis of the interface between hard and soft materials.

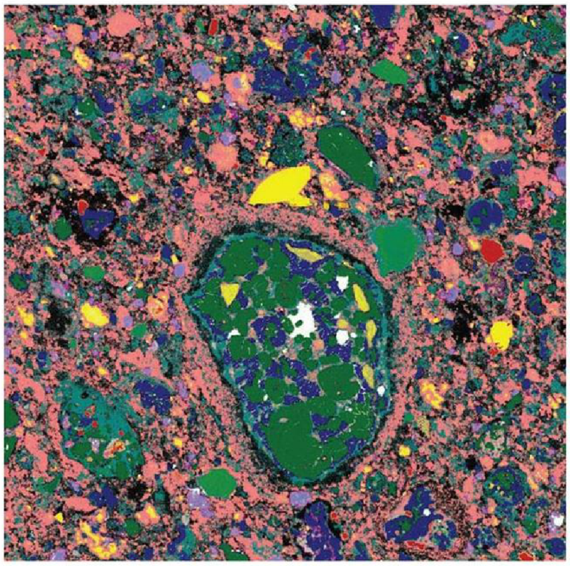
MEETING THE DEMANDS OF THE FUTURE

There will be continuous advances in microscopy that hold the key to solving many of today's and tomorrow's challenges, whether it be medical research, improved structural materials, or energy applications, such as power generation, storage, and efficiency enhancements.

Medical research. Cryo microscopy, named by Nature magazine as the "Method of the Year" in 2015, is gaining a foothold in both life and physical science applications due to its ability to minimize beam interaction effects. Challenges of producing thin, amorphous ice and maintaining it in this state are being overcome by advances in specimen preparation and cryogenic TEM specimen holder technology.

The application of microscopy in the life sciences will continue. In situ experimentation will involve frozen, hydrated materials; the use of liquid cells; mechanical probing; and electrical and magnetic biasing - all of which will yield an understanding of the most fundamental properties and interactions.

FIGURE 5 Shale sample prepared by broad beam argon ion milling



Power generation and storage. The energy sector represents huge opportunities for electron microscopy in areas of power generation, as the development of more efficient fuel and solar cells will continue to be a priority.

Beyond the generation of power, there is an increasing need for energy storage. Microscopy supports various aspects of battery technology, particularly lithium ion batteries. In 2013, microscopy was used to define the problem and affect a solution to the defects plaguing the Boeing 787 Dreamliner's lithium ion batteries. The safety risk presented by the battery problem forced the grounding of the entire fleet of aircraft until a solution was implemented.

While the Dreamliner's lithium ion battery problems have been solved, a current challenge facing microscopy is to develop a method for limiting the exposure of reactive materials (such as those used in lithium ion batteries) to ambient.

Battery technology is being used in automotive applications by companies such as Tesla, which developed the 21st century's first all-electric car.

As we all have become so dependent on our mobile devices, increased battery life is a significant aspect of the technology.

Through the use of GaN, combined with In (InGaN) and Al (AlGaN), energy efficient LEDs have become the light source of choice in many of our homes. With its higher efficiency, power demands are reduced, which results in a net energy savings.

Since the deployment of horizontal drilling and hydraulic fracturing in the 1990s, major advances have been made in the exploration and production of oil and natural gas. SEM has become a highly valuable technique for determining the porosity in the organic phase of the rock. It is within the pores that the oil and gas are resident. Determining the size of the pores and their corresponding connectivity helps geologists determine where to drill a well with the goal of selecting fields that potentially possess the highest production yield (Figure 5 and Figure 6).

Catalysis will remain important for use in the fossil fuel and automotive industries to protect the environment by scrubbing detrimental byproduct gases.

Structural materials. From the research perspective, one needs to consider the useful elements of the periodic table. Understanding the properties and reactions of combined elements will yield the answers to many of today's materials challenges.

Microscopy will continue to support the development of structural materials that are used in construction and infrastructure projects that must be built to withstand a wide variety of climates, natural disasters, geographies, and topographies. For these applications, understanding and altering materials properties leads to advances in material strength, as well as resistance to corrosion and temperature changes.

Transportation. The transportation industry benefits greatly from materials advances afforded by the electron microscope. This pertains to the automotive, aeronautic, and aerospace industries where the drive is toward stronger, lighter materials, and in some cases, materials that maintain their properties at elevated temperatures. This requires an understanding of the properties of the base materials, the properties of the coatings applied to the base materials, and what happens at the interface where the base properties and the coatings meet.

Communication. The semiconductor and data storage industries underpin advances in communication technology and represent a huge market for electron microscopy.

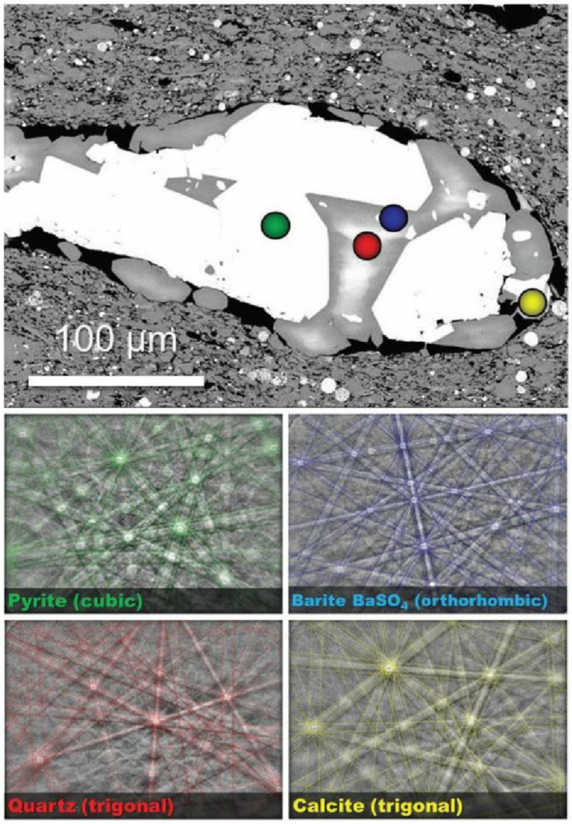


FIGURE 6 The shale sample (top) was mechanically polished down to 1 µm diamond paste, followed by broad beam argon ion milling at 6 kV, 2° beam angle for 60 minutes. Four areas of interest were selected for EBSD analyses. EBSD data were collected at 20 kV, using 1.5 µm step size, 40 Hz acquisition speed (4 x 4 binning); a 96% hit rate was achieved

Currently, massive amounts of data are being pushed, pulled, and stored, with the World Wide Web, smart phones, and electronic devices driving demand.

Data are stored both locally on mobile devices and are also being pushed and pulled from cloud storage. Storage density has increased in terms of both flash memory and solid state drives. Materials challenges increase proportionally as device sizes shrink and layer quantities increase.

Advanced materials are integral parts of both logic and memory integrated circuits, as well as display technology (Figure 7 and Figure 8).

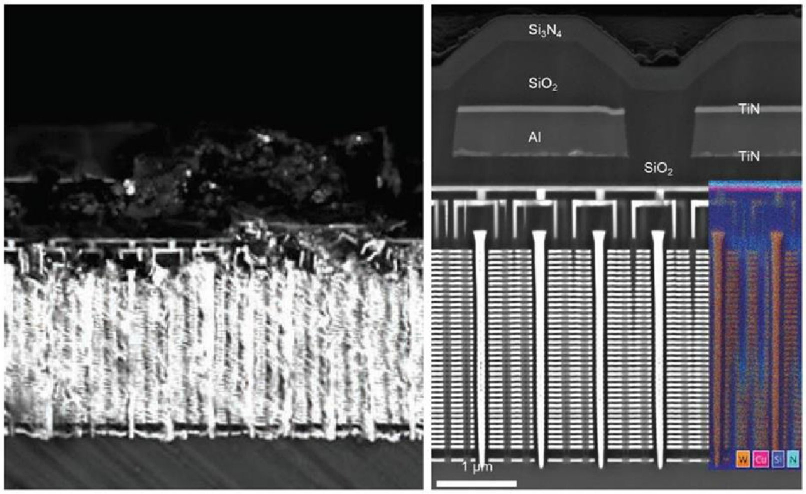


FIGURE 7 Cross-section sample of three-dimensional vertical NAND (3D V-NAND) flash memory. Mechanically prepared sample (left) and the same sample following argon ion milling (right). The highly polished surface post ion milling enables energy dispersive X-ray spectroscopy (right)

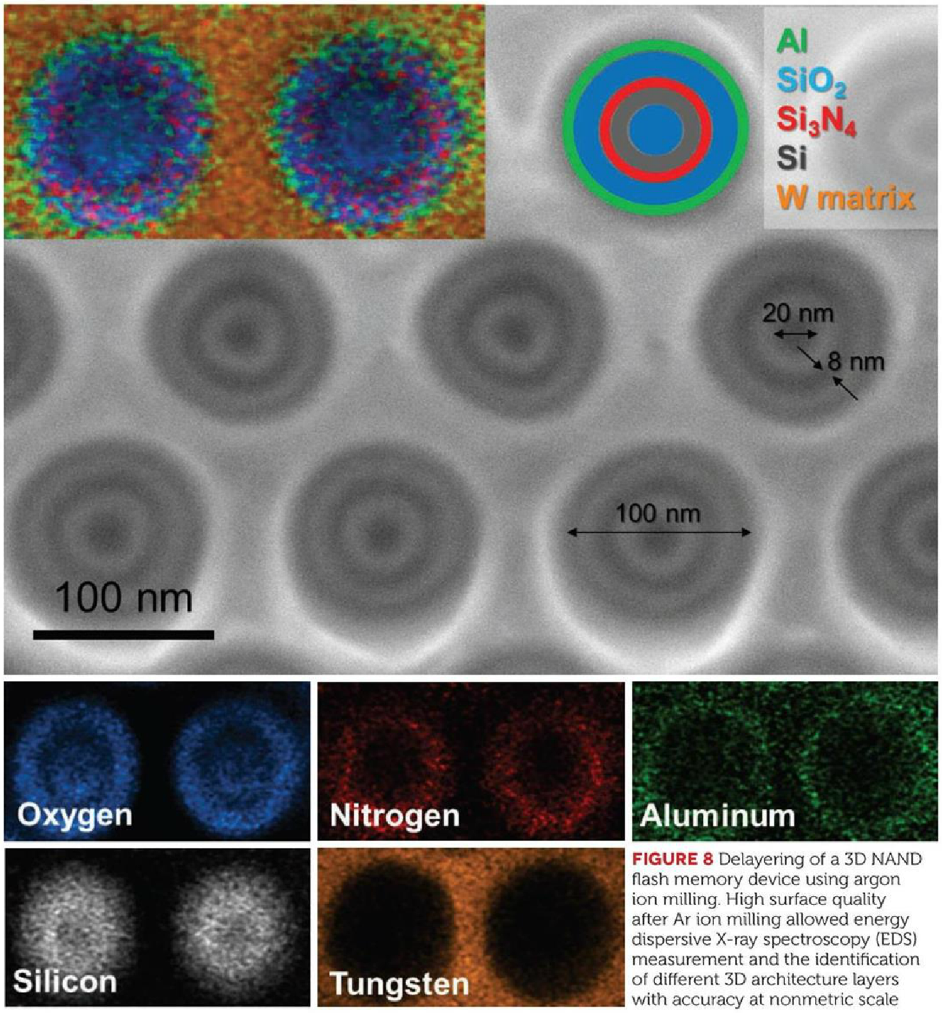


FIGURE 8 Delayering of a 3D NAND flash memory device using argon ion milling. High surface quality after Ar ion milling allowed energy dispersive X-ray spectroscopy (EDS) measurement and the identification of different 3D architecture layers with accuracy at nonmetric scale

At the inception of *M&A*, a transistor node was approximately 1 µm, as compared to the commercially released 14 nm devices of today. Semiconductor manufacturers are expected to ship 10 nm devices this year.

The semiconductor industry continues to try to operate in accordance with Moore's Law. Nodes are shrinking from 14 nm to 10 nm to 7 nm, with a projected 5 nm node on the horizon. At these sizes, aberration-corrected TEM plays a critical role in research, quality control, and failure analysis because it allows atomic-level observation.

Within the recent past, semiconductor devices have gone from two to three dimensions, with a finned field effect transistor (FinFET) being one such example. A single transistor employing FinFET technology now possesses multiple layers comprised of various elements and having thicknesses of just a few atoms. Current integrated circuit technology possesses roughly seven billion of such transistors. Beyond 5 nm device structures, a technological shift away from silicon-based devices may be required. Varied materials and structures such as graphene and nanotubes are now in the fundamental research phase.

Next generation televisions and mobile phones will benefit from organic light emitting diode (OLED) technology, which allows more vivid imagery while consuming less power.

In the health care field, diagnostic sensing technology, combined with real-time data collection and communication, will give physicians the ability to render high-quality, lower-cost, more patient-centric care.

In 1985, Ernst Ruska reflected upon the evolution of microscopy and said, "The light microscope opened the first gate to microcosm. The electron microscope opened the second gate to microcosm. What will we find opening the third gate?"

The future…let's go for it.

BIOGRAPHY

Paul Fischione has played a significant role in electron microscopy for more than 30 years. Fischione is the CEO of E.A. Fischione Instruments, Inc., a privately held, U.S.-based company that designs, manufactures, and distributes advanced microscopy devices. Products include TEM and SEM specimen preparation devices, contamination solutions, and specimen holders. Fischione's professional activities have earned him and Fischione Instruments multiple awards, including the Microscopy Today Innovation Award in 2010, 2011, and 2015; and the Ernst & Young Entrepreneur of the Year (Western Pennsylvania) award in 2013. Fischione currently serves as treasurer of International Federation of the Societies of Microscopy and was named a fellow of the Microscopy Society of America in 2017.

ABSTRACT

There have been substantive changes in the microscopy field over the past 30 years; microscope technology has evolved, the tools and techniques for sample preparation have become more sophisticated, and the material range and depth of characterization have expanded. With each advancement in microscope performance, sample preparation technology had to improve at the same pace. Continuous advances in microscopy hold the key to solving many of today's and tomorrow's challenges, whether it be medical research, improved structural materials, or energy applications, such as power generation, storage, and efficiency enhancements.

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