by Craig S. Schwandt

Characterizing Nanometer-Scale Materials Using a Low-Angle Backscattered Electron Detector

Understanding the properties of new materials prior to fabrication can be challenging. Often, the structure of a material at very small scales is critical to its properties and performance. Visualization technologies continue to improve, allowing scientists to investigate solid materials at scales closer and closer to the scale of individual atoms. One of the most exceptional aspects of scanning electron microscopy is the ability to investigate relatively large samples, such as those that can be held in the hand, with nanometer-scale resolution. Enhancements in electron optics over the past decade have produced phenomenal improvements in secondary electron imaging, which is vital for imaging of surface morphology. More recently, developments in backscattered electron detectors have produced similar improvements in qualitative compositional imaging.

Earlier-generation backscattered electron detectors typically had a resolution of about 200 nm. Thus, even though scanning electron microscopes were capable of much higher resolution using secondary electron imaging, backscattered electron detectors were not able to provide complementary compositional images. However, the latest-generation electron backscattered detectors, coupled with new electron optics, yield compositional images with much higher resolutions. These new detectors produce qualitative compositional maps with nearly the same spatial resolution as secondary electron images, and provide a means of targeting the electron beam for X-ray spectrometer measurements for quantitative analysis.

One such instrument is the low-angle backscattered electron (LABE) detector offered by **JEOL USA, Inc.** (Peabody, MA),[1] which is an option on the company's field emission scanning electron microscopes (FESEMs). An example of an interesting material that can be imaged with the LABE detector is a new type of wound care dressing composed of silver-coated fibers. Silver has gained renewed interest as an antimicrobial weapon, especially with the overuse of antibiotics. The dressings use silver nanoparticle coatings on fibers to provide antimicrobial activity.

Scanning electron microscopy

All scanning electron microscopes (SEMs) have features in common, though they vary in their degree of complexity. The common parts include a source of electrons with a means to accelerate the electrons toward the sample, a lens system to focus the electrons into a beam, an aperture to refine the beam further, a lens to focus the beam to a fine probe, scanning coils to scan the beam over the sample, and detectors to detect the signals generated by the interaction between the electron beam and the sample. Images are formed by scanning the beam over the sample, like reading the lines of a book, and collecting the electron signals generated in synchronized fashion with the scanning. Two basic types of electron signals are commonly detected: secondary electrons and backscattered electrons. It is important to understand the difference between the two types because images produced by each one present different information about the sample. Ideally, the greatest information about a sample is available when images from both signal types are acquired with exactly the same conditions and compared with matched image sets acquired at different beam conditions. Following is a brief explanation of each type of image.

Secondary electron images

Secondary electrons are generated when the electron beam from the SEM strikes the sample and ionizes the atoms of the sample. This interaction depth is very shallow, with most of the detected secondary electrons originating from very near the surface of the sample. Thus, secondary electron images (SEIs) provide images of a sample's surface morphology. The energy of secondary electrons is relatively low. As a result, if the sample is a poor electrical conductor, then electrons from the beam begin to accumulate around the location of the electron beam's contact with the sample; this is commonly referred to as "charging." Charging degrades the image significantly because it can deflect the beam and disturb collection of the secondary electrons by the secondary electron detector. Brightness and contrast of secondary images is primarily a function of the electron flux or dose of the beam, and the sample morphology relative to the secondary electron detector. The ultimate resolving power or the ability of the microscope to distinguish the distance between two very closely spaced objects is primarily a function of the diameter of the beam and the ability of the microscope to raster the beam very precisely at small distances. In both cases, smaller beam diameters and rasters result in higher magnification and image resolution.[2]

Backscattered electron images (BEI)

Backscattered electrons are electrons from the SEM beam that strike the atoms of the sample and are ejected back out of the sample. This interaction occurs at deeper depths in the sample than secondary electron generation. One of the most important aspects about the production of backscattered electrons is that the number of electrons backscattered is proportional to the atomic number of the atoms comprising the sample. Higher-atomic-number elements have larger effective diameters for backscattering and therefore bounce back a larger number of beam electrons than lower-atomic-number elements. Thus, typical compositional mode backscattered electron images are actually qualitative compositional maps. Portions of a backscattered electron image that are bright have a higher atomic number than darker portions of the image.[2]

Image resolution and quality

Although the quality of SEM images is dependent on the quality of the detectors used, there are aspects of SEMs that affect their overall spatial resolving capability and the quality of images they can produce. Several of these factors do not depend on the qualities of the detectors used. These include magnification and scanning stability, that is, the ability to focus an electron beam with a small diameter, and the ability to produce an electron beam with a high electron flux, or bright beam. SEM

manufacturers have been improving these microscope functions for decades, and certainly these improvements have been especially visible in secondary electron imaging capabilities. However, improving the imaging of backscattered electrons has been a more challenging task primarily due to the physics involved.

Before discussing backscattered electron imaging, a few definitions pertinent to imaging overall are necessary. Magnification is the ratio of the horizontal scan or raster distance of the SEM's imaging window (cathode ray tube monitor on old SEMs, but simply an imaging window of the software interface of modern SEMs) divided by the horizontal distance of the beam scan or raster. With recent technology, the beam can be scanned to finer and finer distances. The latest-generation FESEMs routinely support magnifications of one million times with the ability to resolve the distance between two objects spaced at about 1 nm (1×10^{-9} m). The distance between individual atoms is only another factor of 10 smaller. Rastering a tiny diameter beam can be accomplished repeatedly and stably. This requires high precision of the scanning coils. The ability of the scan coils to precisely scan the beam very slowly while the detectors concurrently sample the generated electron signal a sufficient number of times per scan to produce an image with a large number of pixels results in a high-resolution image.

In order to take the greatest advantage of the extremely fine scanning capability, one requires an extremely fine probe. Therefore, the ability to focus a beam with a very fine diameter onto the sample will produce an image with greater spatial resolution than one with a much larger beam diameter. Also, accomplishing this at lower beam energies, or accelerating voltages, whereby the interaction volume is relatively closer to the surface, produces even more clarity because the secondary and backscattered electrons interact with less sample material. At lower beam energies, the smaller interaction volume means that the resolution of backscattered images is much closer to the resolution of secondary electrons.[3] However, since the number of generated signal electrons is smaller at lower energies, actually visualizing both signals at nearly the same resolution required the invention of new electron optics. The new optics are essential not only for high-resolution secondary electron imaging, but also for high-resolution backscattered electron imaging.

Better imaging facilitated by key new technologies

Historically, secondary electron imaging has been capable of 10–100× better resolution than backscattered electron imaging. A major reason for this is that secondary electrons are lower-energy electrons and can be attracted to a conventional secondary electron detector. In contrast, the higher-energy backscattered electrons cannot be similarly attracted, so that once one produces a very fine beam and rasters it over smaller distances, the overall number of backscattered electrons captured is too low to be useful.

A recent advance in the latest FESEM electron optics is the semi-in-lens objective lens, which focuses the beam to a sharp spot. The magnetic field of the semi-in-lens actually extends below the pole piece onto the sample surface.[2] The presence of the magnetic field around the

area of observation assists with collection of the secondary and backscattered electrons. Electrons from the sample follow spiral paths in the magnetic field on their way to a detector. Secondary electrons, which are low energy, spiral with a small, tight radius, whereas higher-energy backscattered electrons spiral with a larger radius.[4] This collection process provides enough signal boost so that the FESEM can be optimized for the finest resolution using low accelerating voltage, or beam energy, and low probe current to avoid charging and damaging the sample, which is most desirable for real-world nanometer-scale samples. The physics of the beam and sample interaction means that low-energy/low-current operating conditions produce smaller interaction volumes closer to the sample surface, and provide the best resolution, but reduce the number of signal electrons to the sample. To accommodate this, in-lens detectors utilize shorter working distances than conventional SEMs.

In-lens detectors for the acquisition of secondary electrons have been in existence longer than in-lens backscattered electron detectors. The latter required a means of separating the two types of signal electrons from one another, because utilizing the extraction enhancement of the final semi-in-lens objective magnetic field accelerates both types of electrons up the lower portion of the column. The two types of electrons can be sorted with the use of an energy filter or electrostatic lens based on the energy of the signal electrons. The lower-energy secondary electrons extracted from the sample travel up the column and are collected by the secondary electron detector, whereas the higher-energy backscattered electrons continue up past the secondary detector toward an in-lens backscattered detector. However, prior to the backscattered detector, the electrons encounter an energy filter, or electrostatic lens, which precludes secondary electrons and allows only backscattered electrons to pass up to the in-lens backscattered detector. The in-lens detectors acquire secondary and backscattered electrons that have a high take-off angle and small magnetic field radius from the sample. As a result, in-lens detectors are most useful for high-magnification, short-working-distance imaging at low beam energies. In these situations, the resolution of the in-lens backscattered detector can approach that of the secondary electron imaging because the lower beam energy results in a smaller sample interaction volume nearer the sample surface. Because older-style annular backscattered electron detectors had no means of enhancing collection of backscattered electrons, their resolution is lower by at least 100-fold.

LABE detector

A new type of annular backscattered detector specifically designed to work at intermediate working distances of 4–8 mm is the low-angle backscattered electron detector.[1] The advantage of this detector is that it is able to collect backscattered electrons that leave the sample at lower angles, in other words, electrons with a larger radius in the magnetic field of the semi-in-lens objective lens.[4] As a result, the LABE detector is more sensitive to surface information. The ability of the semi-in-lens objective lens magnetic field to contain and focus the low-angle backscattered electrons is noteworthy. The resolution of the LABE detector in the working world is functionally equivalent to the secondary image resolution, down to

Figure 1 SEI of wound-care dressing fibers coated with nanometer-scale silver. Beam energy is 5 kV.

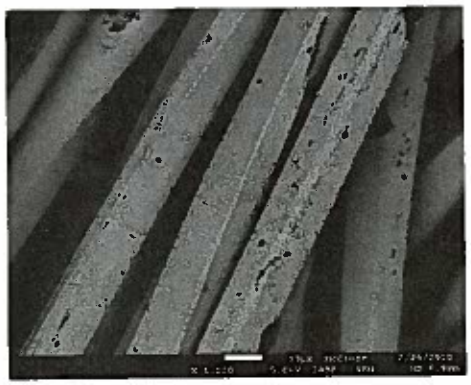

Figure 2 Backscattered electron image acquired using the LABE detector corresponding to the SEI image shown in Figure 1. The silver coating on the fibers is represented by the much brighter gray, while the underlying organic polymer is represented as black. The 5-kV beam energy is moderate to low, but signal-to-noise is very good, producing an aesthetic image.

at least 5 nm. Special cases may be able to achieve even better resolution.

Another technological advantage allows the LABE detector to achieve fine-scale resolution, particularly at low beam energies. This is accomplished by a feature called "gentle beam" mode. Gentle beam mode places a negative bias charge on the sample stage and sample. This process both retards the electron beam to provide a beam that is tightly constrained by higher-energy conditions through the FESEM column—but which lands on the sample with a much lower energy, thus producing a small near-surface interaction volume—and also accelerates the signal electrons toward the detectors.[4] Thus, the LABE detector is capable of producing qualitative compositional images with a very high degree of atomic number contrast. Under certain circumstances, such as when dealing with nonconductive samples, the LABE detector actually functions better than the secondary electron detector, because the higher-energy backscattered electrons are less affected by charging of the sample by the electron beam.

Utility for nanotechnology

Throughout the course of research and development of new products, test examples of the product often do not perform as expected. In order to determine why they perform in ways other than expected, they must be inspected to determine the mechanisms resulting in the behavior. Today's research and development looks toward nanometer-scale materials as a new frontier for developing new products. However, when products utilizing nanometer-scale materials fail, an analysis tool that is capable of visualizing the materials is required. The latest-generation FESEMs with backscattered detectors are well suited for this task. Determining the properties of a new material requires the ability to see the morphology, composition, and structure of the materials in situ. The qualitative compositional imaging of the LABE detector is critical for focusing the electron beam of the FESEM on the correct volumes of interest at the nanometer scale, so that other detectors can be utilized to acquire compositional and structural information.

One area currently experiencing rapid growth is the production of materials with antimicrobial properties. The concept is highly desirable because the materials eliminate the need for potentially poisonous and messy wet chemicals, which are applied as coatings or washes. In some instances, it is the structure of

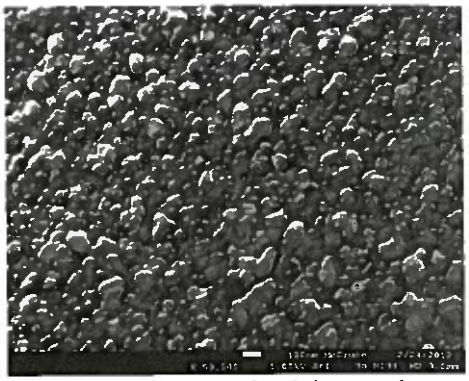

Figure 3 The topography of silver particles is evident in this SEI image at higher magnification than Figure 1. Particles smaller than 10 nm are distinguishable from the larger particles. Note that the beam energy is now only 1 kV; thus the interaction volume is near the surface of the sample.

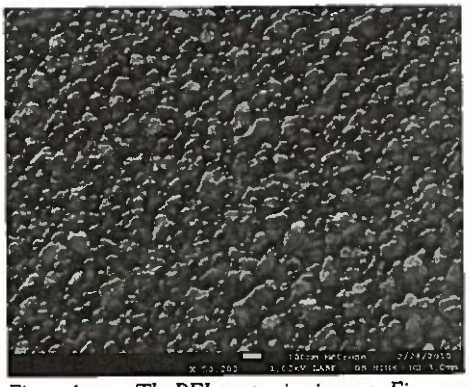

Figure 4 The BEI companion image to Figure 3 produced by the LABE detector demonstrates that most of the silver particles that are 10 nm and smaller are distinguishable at 1-kV beam energy with a very good signal-to-noise ratio. Compositional and topographic information is captured by the LABE detector. Capture of images with these qualities was not possible with earlier-generation instruments.

solid materials applied to the surfaces of other materials, and in other cases it is the material itself, like silver, that acts as the antimicrobial agent. Silver has long been used because of its antimicrobial properties, but is receiving renewed interest with the incorporation of silver nanometer-scale particles on fabrics and other solids. The exact antimicrobial mechanism of silver has not been entirely determined, and appears to function differently in different uses, but it has been demonstrated to be effective in many instances.[5–8]

An example that demonstrates the capabilities of the LABE detector is examination of the fibers of a silver-coated wound care dressing. In this example, the fibers are completely coated by nanometer-sized silver particles to

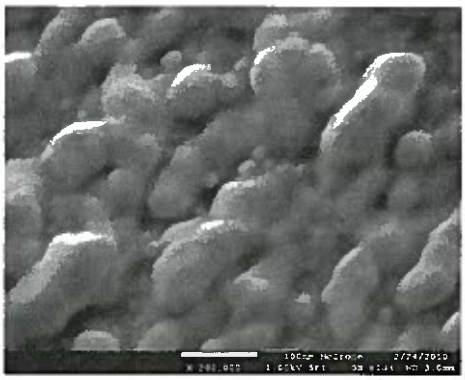

Figure 5 At 200,000 times magnification at 1-kV beam energy, other effects are captured in the SEI image. Horizontal lines are visible that result from sample charging and environmental noise around the FESEM.

the extent that the fibers have a metallic gray color. The dressings reportedly decrease the healing time required, especially when used in the treatment of burns. Images of the dressing fibers are shown as secondary and backscattered electron image pairs to provide as much information as possible—the fine surface morphology provided by the secondary electron image and the compositional information provided by the backscattered electron image. In this case, the backscattered electron images reveal the homogeneity of the silver coatings. However, the image pairs also demonstrate the resolving power of the LABE detector. The images have equivalent resolution to the secondary images.

Figures 1 and *2* are low-magnification images that show small portions of polymer fibers coated with nanometer-scale silver. *Figures 3–6* are high-magnification images of the nanometer-scale silver particles on the surface of the fibers. At the highest magnifications, environmental effects (vibration, magnetic fields, etc.) of the laboratory often limit resolution, rather than the capability of the microscope (e.g., Figure 5).

Conclusion

The latest-generation FESEM instruments are up to the challenge of characterizing nanometer-scale materials. Samples that can be held in the hand can be examined at single-nanometer resolution without adulteration by sample preparation techniques.

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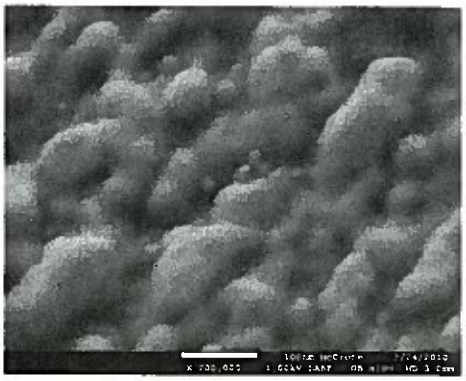

Figure 6 The BEI companion to Figure 5 demonstrates that particles smaller than 10 nm can be resolved by the LABE detector at 1 kV beam energy.

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