APPLICATION NOTE

ChemiSTEM Technology

A revolution in EDX analytics, reducing analysis time from hours to minutes

Nanoscale chemical composition is pivotal for understanding nanostructures and devices. Now, previously hidden features and elements can easily be detected with ChemiSTEM Technology, providing answers to long-standing questions.





ChemiSTEM Technology: A revolution in X-ray analytics

X-ray spectroscopy is a well-established, robust and easy-touse technique for obtaining nanoscale detail of nanostructures and devices. Scanning/Transmission Electron Microscope (S/ TEM) X-ray analysis pairs microstructural details obtained from high-resolution imaging with accurate chemical composition data. X-ray analysis has, however, been historically limited with S/TEM: only about 1% of all X-rays generated by the beam are collected. Recently, as the desired spatial resolution of chemical analysis has become progressively greater, the X-ray signal has decreased even further, as fewer atoms are excited in the small analytical volume (the result of smaller beams and thinner samples). This results in low signal strength, which brings about low sensitivity and hence long analysis times—until now.

Thermo Scientific[™] ChemiSTEM[™] Technology has been developed over a five-year period with the express purpose of removing old performance barriers, bringing orders-ofmagnitude improvement to many key metrics, such as sensitivity and speed. This reduces analysis times from hours to minutes, and sample features and elements that previously remained hidden can now be detected easily. With this new technology, we believe X-ray analytics in the S/TEM is poised to experience a renaissance. We begin with an explanation of how ChemiSTEM Technology is able to provide such breakthrough capabilities.

Introduction to EDX analytics and ChemiSTEM Technology

Modern X-ray analysis on the S/TEM employs a well-established technology called X-ray energy dispersive spectroscopy (EDX). In this technique, the electron beam ejects atomic core-shell electrons in the sample; a higher shell electron fills the now empty core state, creating X-rays with the atom's characteristic energy. These X-rays are absorbed by a nearby semiconductor detector; the deposited X-ray energy creates between a few hundred to a thousand electron-hole pairs, which are immediately separated and collected by the detector as a

charge pulse. The fast electronics used to accurately detect these pulses are robust and reliable, meaning they produce highly-repeatable results with easily calibrated energy. The pulse-processing electronics measure the area under each pulse (a.k.a. X-ray count, which gives energy) and then each is "binned," resulting in a spectrum of characteristic peaks. These can then be automatically labeled by the computer. As noted, this technology is simple to use and reliable, but suffers from the very small volume analyzed and poor ~1% total X-ray collection efficiency. We analyzed this limitation and realized that, in order to create a game-changing new capability, we would need to achieve an orders-of-magnitude boost in the net X-ray count rate. Total improvements of 30% or even a two- to three-fold increase would simply not be revolutionary.



Figure 1. A schematic of the ChemiSTEM Technology design, showing the X-FEG high-brightness, Schottky electron source, and the Super-X System geometry including four SDD detectors arranged symmetrically around the sample and the objective lens pole pieces. This schematic is not to scale.

It was clear a radical new X-ray detection system would be needed, but we also realized that net X-ray count rate depends not just on the collection efficiency (set by the detector system) but also on the count generation rate (set by the beam current). The ChemiSTEM Technology design, which addresses both these needs, is shown in Figure 1. The higher beam current is provided by the proprietary X-FEG (extreme field emission gun) Schottky electron source, which can generate up to five times more beam current at a given spatial resolution compared to a conventional Schottky FEG source. The higher efficiency detection system is a brand new concept; our integrated Thermo Scientific[™] silicon drift detectors (SDDs) are very close to the sample area (these detectors are windowless to further boost collection efficiency and light element detection capability). This proprietary EDX design is called the Thermo Scientific™ Super-X[™] System. Compared to conventional single-SDD Schottky FEG systems, the ChemiSTEM Technology produces up to five times the X-rays with the X-FEG, and up to 10 times the X-rays are collected with the Super-X System. Additionally, compared to conventional Si(Li)-detector Schottky FEG systems, there is multiplicative speed enhancement due to the increased speed of the new SDD detectors. Figure 2 shows the results of an analysis time benchmark test; the Tecnai Osiris

S/TEM (with ChemiSTEM Technology), formerly produced by FEI, was compared to a conventional 200 kV S/TEM with the same sample. The conventional S/TEM was equipped with a Schottky FEG and Si(Li) detector at 0.3 sr (steradian) X-ray collection angle. The acquisition times were adjusted to achieve comparable X-ray statistics on both systems. For equivalent EDX map sizes and statistics, the results took just under 2 hours (1 hour 54 min) on the conventional system and just under 2 minutes (115 sec) on the system with ChemiSTEM Technology, a change from hours to minutes. This demonstrates the magnitude of ChemiSTEM Technology's raw speed advantage, but the benefits of this method extend further to previously unobtainable results, including:

- Detection of 0.02 wt.% elemental concentrations
- Identification of a catalyst core shell structure in 4 minutes
- 800x800 pixel structural overview maps in 78 seconds
- Fully quantified 600x600 elemental maps in about an hour with a pixel resolution of 0.3 nm
- Never before seen levels of light element detection (eg. C, O, N)
- All these examples will be explored further, starting on page 9.



Figure 2a. 1 hour 54 minute total map acquisition time. 100x100 pixel EDX map of a semiconductor device taken on a Tecnai TF20 XT TEM (0.3 sr Si(Li) system) with 500 msec/pixel dwell times, ~0.7 nm spot size, 0.4 nA beam current. Sample courtesy of NXP Research, maps by D. Klenov, A. Carlsson, Thermo Fisher Scientific.





Figure 2b. 115 seconds total map acquisition time. 100x100 pixel EDX map of an equivalent semiconductor device taken on a Tecnai Osiris S/TEM with ChemiSTEM Technology with 5 msec/pixel dwell times, ~0.3 nm spot size, 1.0 nA beam current.

The Super-X System advantage: Tilt response

The major advantage of the Super-X System design comes from the large solid angle for X-ray collection provided by four SDD detectors, symmetrically arranged around the specimen. Specimen tilting is, however, another important advantage. Figure 3 compares measured X-ray count rates over a tilt range from -25° to +25°, for a Super-X System with 0.9 sr solid angle (red curve) and for a system with single Si(Li) detector with 0.3 sr solid angle (blue curve). The count rates (integrated over the entire energy range) were measured at 200 kV using standard commercially available NiOx test films with nominal thickness of 50 nm \pm 10 nm. The Super-X System response never drops below 80% of the maximum count rate over the entire tilt range. By contrast, the single detector system only achieves its maximum count rate when the sample is tilted strongly to +20° towards the single detector. At zero-tilt, the count rate is already reduced by 30% or more (due to geometrical shadowing of the single detector by the sample holder), and at negative tilt angles, complete shadowing occurs at -10°, where the response drops to zero. All one-detector systems suffer from a similar undesirable tilt response, which occurs equally for SDD or

Si(Li) detectors. The superior Super-X System response occurs because at any tilt angle there are at least two detectors almost fully illuminated, and the 2 other detectors > 50% illuminated. Super-X System response to beta tilt angles (not shown) is very similar to the results in **Figure 3**.

The ability to achieve high X-ray signal over a large portion of the S/TEM tilt space is a key performance improvement of the new system. Many studies in material science or chemistry require tilting to angles that cannot be easily controlled a priori due to the unknown orientation of nanoparticles or grain boundaries in poly-crystalline material. In these cases, the sample can be tilted to optimize imaging conditions and subsequently does not need to be re-adjusted for optimum EDX analysis conditions. Conversely, an important crystal orientation is often prepared to be close to zero degrees tilt for many samples. In these cases, it is clearly a key advantage to have the maximum X-ray response at zero tilt, as opposed to the observed ~30% response reduction caused by shadowing. In these cases, it may not be feasible to tilt the sample towards the single detector to maximize response, due to the need to keep the beam parallel to a material interface (for an edge-on view).



Figure 3. Comparison of relative EDX count rates of the Super-X System (on Tecnai Osiris S/TEM with 0.9 sr collection angle) and a single Si(Li) detector system with 0.3 sr nominal solid angle. Both S/TEMs were operated at 200 kV with the same (constant) beam current. NiOx films were used as samples for both tilt series. The count rate is normalized to unity at the maximum response of the Super-X System, occurring at zero tilt angle. Positive tilt angles represent specimen tilts towards the single detector for the Si(Li) system. Diagrams above the graph show the effects of detector shadowing for the four Super-X System detectors, and diagrams below show shadowing effects for the single-detector system.

The Super-X System advantage: Total response (1+1+1+1 > 4)

By simple logic, one expects the Super-X System with four detectors to be four times better in response than a onedetector system (i.e., 1+1+1+1 = 4). However, this is not the case, as each individual Super-X System SDD detector has significant design improvements in and of itself, compared to conventional single-SDD detectors. This essentially means that the response of each Super-X System detector is >1. We can then ask, "How much greater?"

There are two major design improvements for individual detectors, leading to three distinct response improvements. First, as described earlier, since Thermo Fisher Scientific designed the individual Super-X System SDD detectors to be optimized for the Thermo Scientific objective lens pole piece design (shape, size, geometry, etc.), we were able to completely eliminate the problem of detector shadowing at zero tilt angle. This means that the detector sits at a "take-off" angle/location and is fully illuminated at zero tilt with no shadowing loss. This required the design of a special sample holder, as well as an optimized detector design.

Second, the Super-X System detectors are windowless by design. Instead, they have mechanical shutters that completely protect them when they are not in live mode. This eliminates the need for ultra-thin polymer windows, which are typically a source of two distinct severe response losses. **Figure 4a** illustrates these effects. First, the polymer film itself is supported by a



Figure 4a. Schematic showing loss due to holder shadowing and detector window. Loss due to the window includes total absorption by the Si support grid bars (at all energies) and selective absorption by the polymer window (at energies below 1 keV).

silicon support grid, which blocks all X-rays hitting it; this results in a substantial X-ray response loss for all energies. Second, the polymer windows themselves, although transparent to X-rays >1 keV in energy, do have substantial absorption loss below 1 keV, particularly due to the carbon absorption edge around 300 eV, as seen in **Figure 4b**. Clearly, there is a significant efficiency loss caused by the windows (lower blue curve) as compared to a windowless system (upper red curve). The remaining loss in the windowless system, below 1 keV, is due to residual absorption by the thin Al electrode and Si dead layer at the front of the SDD detector. The windowless system has a factor of at least two to three times greater efficiency at energies below 500 eV. This improvement in low-energy X-ray collection efficiency has a huge impact on light element detection, as we will discuss in a later section.

We estimate that a typical conventional system has ~50% loss of its nominal solid angle response at zero tilt because of the described loss mechanisms. Thus, the expected zero-tilt efficiency increase of the Super-X System would be a factor of ~8: the four detectors plus an additional factor of ~2 to account for the 50% loss. This comparison assumes one detector of nominally equal solid angle to the individual Super-X System detectors. The additional efficiency gained by the Super-X System at low energies (below 1 keV), due to the lack of polymer window, is not included. Clearly, the exact efficiency enhancement depends on many actors, including tilt angles employed, nominal solid angle differences, low-energy enhancements, etc.



Figure 4b. X-ray transmission efficiency for a windowless SDD detector (red curve) and an SDD detector with thin polymer window (blue curve). Loss due to the both the Si grid bars and the polymer window contributes to the lower efficiency across all energies of the detector with window.

In general, we find that the collection efficiency shown in actual experiments with the Super-X System is between 5-10 times greater than with existing conventional EDX systems. The one exception is efficiency comparisons well below 1 keV, where the enhancement factor is >10.

How to compare collection efficiencies of different EDX systems

The traditional S/TEM metric for judging EDX collection efficiency is to use the "nominal" solid angle. By this, we mean the pure geometrical solid angle, subtended by the detector, viewed from the eucentric sample point, and based on only the detector's cross-sectional area and distance from the eucentric point. This does not include loss from effects such as detector shadowing or windows, which make quite a difference. Sometimes, non-active detector areas such as metallic guard rings will be included when calculating nominal solid angle. True efficiencies thus depend on a range of unknown parameters (sample holder geometry, detector elevation angle, etc.) that cannot always be realistically obtained by users. We propose that the most accurate way to compare EDX system efficiency is by measuring actual X-ray count rates per applied beam current using a standard sample of known thickness.



Figure 5. Input count rate for ChemiSTEM Technology (red curve) compared to standard technology consisting of Schottky FEG + 0.3 sr Si(Li) detector (blue curve). For details see text.

This method of comparison is shown in Figure 5. Input counts per second (cps) are plotted as a function of applied beam current for two S/TEM systems: A Tecnai Osiris S/TEM with ChemiSTEM Technology and a 200 kV S/TEM with Schottky FEG and Si(Li) detector of 0.3 sr nominal solid angle. For both measurements, the same FIB-cut InP sample was measured and the X-ray counts were integrated over the full energy range. In order to be sure all measurements were taken on sites of the same thickness, EELS was employed to control sample thickness by measuring t/λ (thickness in relation to average mean free path). The first point of interest is that the Tecnai Osiris S/TEM achieved more than five times the collection performance of the conventional system, despite the fact that it is considered high-end. Second, much higher (>10x) beam currents can be applied on the X-FEG ChemiSTEM Technology system without saturation of the Super-X System detectors. At an applied beam current of 10 nA, the input X-ray count rate is over 400,000 cps for the Super-X System detector at 50% dead time, meaning that the actual output X-ray count rate is over 200,000 cps at this applied current. The Super-X System has significantly higher input bandwidth for high count rates compared to systems with only one high-speed SDD detector, This means that the Super-X System can operate at 400,000 cps input count rate without significant degradation of energy resolution, which is not the case for systems with only one high-speed SDD detector.

The ChemiSTEM Technology advantage: Light element sensitivity

Poor detection of light elements (such as carbon, oxygen and nitrogen) has always been considered one of EDX's major weaknesses, but ChemiSTEM Technology has overcome this barrier. As shown in **Figure 4b**, the relative sensitivity of the windowless system for low-energy X-rays (500 eV or less) is several times higher than for systems with ultra-thin polymer windows. This low-energy advantage, when combined with the 5–10-fold collection increase for the Super-X System, results in an order-of-magnitude boost in light element detection.

Figure 6 shows measured data that demonstrates the enhanced low-energy performance of the Super-X System. The count rates of a NiOx film measured with both the windowless Super-X System and conventional EDX system are normalized (set equal) at the Ni-K line (7.4 keV) in order to highlight only the relative differences in low-energy efficiency. The advantage of the windowless system can clearly be seen in the higher counts of Ni-L, O-K, and C-K lines below 1 keV. The relative peak height is more than two times greater for oxygen at 528 eV and more than three times greater for carbon at 282 eV than for the system with polymer windows. We stress that this comparison does not include the primary Super-X System collection efficiency increase (which is energy independent) since this has been removed in Figure 6 by normalization. For a dramatic demonstration of the ChemiSTEM Technology light element performance, see the C, N and O maps shown in the PMOS transistor structure example found later in this note.



Figure 6. Comparison of a single windowless SDD with a standard Si(Li) detector with ultra-thin polymer window. The two spectra have been normalized to each other at the Ni-K line so that relative differences in the energy range below 1 keV are apparent.

Ultimate sensitivity: Detection of low concentrations

The improved performance of this new technology can be turned into a huge speed benefit ("hours to minutes") as we have demonstrated, but it can also be used to achieve much higher sensitivities than were previously possible. This is, perhaps, more important than speed, as it allows the detection of previously hidden features and elements. The ultimate test of EDX raw sensitivity is the ability to detect very low concentrations of elements, for example, well below 1 wt.% (weight %).

Figure 7 shows the EDX spectrum of a certified NIST steel standard (Standard Reference Material NBS No. 461). In bulk, this low-alloy steel has certified concentrations of the following elements: arsenic (0.028 wt.%), vanadium (0.024 wt.%), and tin (0.022 wt.%). Although this sample was prepared for TEM analysis using a FIB, it is expected that minimal changes have resulted in the composition. The full spectrum in **Figure 7** was acquired in 600 seconds, using a beam current of 1.7 nA, while scanning a micron-sized area. This was done to average the composition across the steel microstructure. The inset (zoomed) spectra at the bottom of **Figure 7** show clear peaks from these

three elements (V, As and Sn), all of which have substantially good signal-to-noise ratio (Ga and Pt peaks visible are due to the FIB preparation process). This clearly demonstrates that the ChemiSTEM Technology on the Tecnai Osiris S/TEM is capable of detecting low concentrations with a reasonable acquisition time (such as the ~0.02 wt.% concentrations of the steel sample, obtained in 10 minutes total acquisition time).

Whether your applications call for the ultimate speed benefits (while mapping in "hours to minutes," or huge area maps with unprecedented sensitivity in reasonable times), or the pursuit of ultimate sensitivity (pushing the limits of detection for ultralow concentrations or hidden sample features), we believe ChemiSTEM Technology will give you the capability to address many of your unanswered questions. In the following pages of this note, we show application data from the ChemiSTEM Technology on Tecnai Osiris S/TEM, covering many different types of material systems. We hope that this note has been a useful introduction to this revolutionary method, and we invite you to contact us at Thermo Fisher Scientific for further information on this new and exciting capability.



Figure 7. Super-X System spectrum of NIST steel standard NBS No.461 (log scale), Bottom: zoomed spectra showing minor elements of vanadium (0.024 wt.%), arsenic (0.028 wt.%) and tin (0.022 wt.%). Ga and Pt peaks are due to FIB preparation.

Fast acquisition of large maps

Due to the increased sensitivity of the Super-X System and the higher brightness of the X-FEG, it is possible to acquire large area maps with high spatial resolution. This allows you to adopt new and more efficient methods of sample examination. For example, instead of trying to understand elemental distribution from images and then confirm it by point analysis or line profile acquisition, it is now possible to acquire a large map with the speed of a STEM image and subsequently proceed with a more careful analysis. This minimizes the time needed to understand the geometry of the sample, allowing for better understanding of its macroscopic structure. Another important advantage of high-speed mapping is the minimization of beam damage. Often, samples will not be able to survive beam exposure longer than 100 µsec. Using fast iterative mapping prevents damage and allows for more accurate post-acquisition analysis of the chemical composition.



Figure 8. These 800x800 pixel maps show the whole FIB lamellae and were mapped with ChemiSTEM Technology in just 74 seconds using 100 µsec/pixel dwell time. This exposure is similar to what would occur while acquiring a few STEM images, and the resolution of the maps is actually equal or better than some of the HAADF STEM images. Note that even with such a short mapping time, it is not only possible to identify the distribution of heavy elements (like W), but but the signal for elements like N and O (which are usually troublesome for EDX) can also be seen. This light element sensitivity is possible due to the windowless design of the Super-X System.

Sample courtesy of IME, Singapore.

45 nm PMOS transistor structure: Large maps, all elements

Development of semiconductor devices necessitates measurement of all elements present in the device structure so that the success and quality of the process can be closely monitored. In that respect, semiconductor devices are demanding, since they contain heavy elements such as tungsten (W), tantalum (Ta) and hafnium (Hf) as well as light elements as small as nitrogen (N), oxygen (O) and even sometimes carbon (C). This example of a 45 nm PMOS transistor structure (Figure 9) demonstrates the advantages of ChemiSTEM Technology. First, the increased sensitivity to light elements allows virtually all parts of the periodic table to be detected in one EDX map acquisition. Second, these maps were acquired with a 0.3 nm pixel resolution over a large field-of-view (about 190 nm in width). This high-resolution, high field-of-view combination is only possible due to the high brightness of the X-FEG source. You can fully appreciate the advantages of ChemiSTEM Technology by looking at the unprecedented sensitivity and resolution seen in the light element maps of oxygen and nitrogen (Figure 9b).





Figure 9a. 600x600 pixel maps of a 45 nm PMOS transistor structure (AI, Ni, Hf, Ta, W) recorded with 50 µsec dwell time/pixel and 1 nA beam current. Drift correction was applied to acquire multiple frames in 100 minutes. The maps were fully quantified to eliminate contributions from overlapping peaks.

Data courtesy of D. Klenov, Thermo Fisher Scientific



Figure 9b. Figure 9b. 600x600 pixel maps of a 45 nm PMOS transistor structure (Si, Ge, N, O, C, Ti) recorded with 50 µsec dwell time/pixel and 1 nA beam current. Drift correction was applied to acquire multiple frames in 100 minutes. The maps were fully quantified to eliminate contributions from overlapping peaks.

Superconductors

Nb₃Sn superconducting cables have promising applications in NMRs and Tokamak fusion reactors. Their use could provide higher current density at lower cost than current solutions. It is important, however, to know their chemical composition, since it impacts the superconducting properties.

Overview maps were taken from the cross section of the Nb₃Sn superconducting multifilament cable (**Figure 10**). The Sn map clearly shows a variation in composition of the superconducting phase that influences the critical current densities. The compositional changes are caused by the initial interdiffusion of the Sn into the Nb filament from the bronze matrix. This allows direct identification of the best areas for superconductivity.

The analysis also shows that Cu from the filament cladding interdiffuses into the Nb₃Sn filament along the grain boundaries (see **Figure 11**). Although there is only a tiny amount of Cu (not soluble in Nb₃Sn), it is possible to detect it. The map also shows the variation of Sn and Nb composition in the grains.



Figure 10. 400x400 pixel maps recorded with 4 msec dwell time/pixel, 2.5 nA beam current and 1-1.3 nm spot size in 11 minutes. Maps show elements using integrated intesities.

Sample courtesy of Marco Cantoni (EPFL Lausanne, Switzerland)



Figure 11. 400x400 pixel maps recorded with 4 msec dwell time/pixel, 2.5 nA beam current and 1-1.3 nm spot size in 11 minutes. Maps show elements using integrated intesities.

Sample courtesy of Marco Cantoni (EPFL Lausanne, Switzerland)

High-TC superconductors

This sample is a FIB-cut section of a YBCO high transition temperature (High- T_c) superconducting ribbon. These ribbons are designed to carry extremely high maximum current density at ultralow Ohmic energy dissipation (e.g. << Cu wire) for applications such as energy transmission and distribution.

Small concentrations of Nb have been added to this material with the goal of introducing vortex pinning defects that can help increase the wire's maximum current carrying capacity (i.e. critical current). The HAADF STEM image shows nanometer-scale columnar defects running left to right (horizontally) intersecting with the vertical



YCuO and YBCO phases. The Nb EDX map clearly shows the Nb segregation visible as many horizontal Nb columnar features that are unambiguously spatially correlated with (and, in fact, were the cause of) the columnar defects seen in the HAADF STEM image. The low Nb concentrations associated with these columnar features are difficult to see in EDX. The results below were acquired on a Tecnai Osiris S/TEM in ~10 minutes. Similar EDX measurements, showing the Nb columnar structures, took 10+ hours of acquisition time on an S-FEG Tecnai F20 ST TEM (0.13 sr, Si(Li) detector, advanced drift correction techniques to minimize drift).

Figure 12. FIB-cut sample of YBCO high-T_c superconductor. ChemiSTEM maps are 400x400 pixels taken with 2.2 nA beam current, approx. 1.5 nm spot size, 100 µsec dwell time, taken in less than nine minutes (531 sec total acquisition time).

Sample courtesy of Dean J. Miller & Jon Hiller (Argonne National Laboratory) Tecnai Osiris experiments: N.J. Zaluzec (ANL), D.O. Klenov, Thermo Fisher Scientific

Metallurgy

In this example, the power of ChemiSTEM Technology is applied to the chemical composition of metal alloys with phase segregation. With nanoscale phase separation and intergrowth, the mechanical properties of alloys can be tuned in order to influence macroscopic structural properties. In this example the intergrowth of orthorhombic WB into hexagonal TiB₂ dramatically improves the hardness of pure TiB₂. This intergrowth is enhanced by doping of CrB2 into the material. The chromium increases the mobility of the boron lattice, enabling the intergrowth of the monoboride (WB) in the diboride matrix (TiB₂). The WB is growing along the prism planes of the hexagonal TiB₂ matrix, creating a hexagonal pattern in the HAADF images in STEM. The HAADF images show the complexity of the intergrowth on the mesoscopic level (**Figure 13**) and atomic level (**Figure 14**). The smallest WB layers are the size of a WB unit cell, which is approximately 0.8 nm. In the chemical maps, the WB layers can clearly be resolved in the W and Ti map. The smallest lines correspond to a single unit cell of WB. The chromium map reveals the enrichment of the chromium around the WB. The concentration of the chromium is extremely low since only 5% of CrB₂ was added macroscopically to the compound to stimulate WB growth.



Figure 13. HAADF image (upper left) of WB/TiB2/CrB2 compound with corresponding ChemiSTEM Technology maps of chromium, tungsten and titanium. All images were acquired simultaneously. Map size is 512x512 pixels, acquired with 50 µsec dwell time/pixel, 20 min total mapping time and 1 nm spot size. Structures as small as 0.8 nm are visible in the chemical maps.

Ceramics: Porous alumina/titania nanocomposite

Nanostructured titania is highly attractive for a number of current and potential chemical, optical and biomedical applications. A proprietary fabrication process (under development by the School of Materials Science and Engineering, Georgia Institute of Technology, in collaboration with the U.S. Air Force Research Laboratory) has been used to synthesize titania-coated porous alumina nanocomposite structures. The X-ray maps shown in **Figure 15** (obtained by the Department of Materials Science and Engineering, The Ohio State University, with ChemiSTEM Technology on the Tecnai Osiris S/TEM) reveal the controlled distribution of titanium, aluminum, oxygen and phosphorus in the titania/alumina-based composites. Such high-resolution X-ray mapping allows critical correlation of processing changes to nanoscale structures and chemistries. This research is being conducted within the BIONIC (Bio-nano-enabled Inorganic/ Organic Nanocomposites and Improved Cognition) Air Force Center of Excellence, which involved collaborators at the Georgia Institute of Technology, The Ohio State University, and the Air Force Research Laboratory.



Figure 15. 512x512 pixel maps recorded with 50 µsec dwell time/pixel, 1.4 nm spot size, and 2.2 nA beam current in less than 6 minutes (327 sec).

Courtesy of the following cooperation: T. McLachlan, Y. Cai, and K. H. Sandhage (Georgia Tech), D. Huber, R. Williams, and H. Fraser (Ohio State), N.J. Zaluzec (ANL) and M. Durstock and R. Vaia (Air Force Research Lab)

Nanoparticle mapping

ChemiSTEM Technology enables monitoring of nanoparticles as small as 1 nm in diameter. Therefore, it can be used to check quality and repeatability of different nanoparticle production routes. **Figure 16** shows Au particles on carbon substrate, with particle sizes varying between 1 and 2 nm.

Mapping very small nanoparticles is an important application, but sometimes it is necessary to distinguish nanoparticles or clusters of different composition. This can be achieved using HAADF STEM images because their contrast strongly depends on the atomic number (Z) of the elements. However, it is almost impossible to distinguish particles with different composition from HAADF STEM images when the elements' atomic numbers are relatively close (as seen on the HAADF STEM image in **Figure 17**). In this case, ChemiSTEM Technology successfully identified the different metals (Au, Ag, Co, Pd, Pt) that are displayed in the RGB image.



Figure 16. Au particles on carbon substrate, with particle sizes varying between 1 and 2 nm.

Specimen courtesy of NANOGAP, Spain (www.nanogap.es) and the NANOMAG group (www.nanomag.org) of the University of Santiago de Compostela, Spain.



Figure 17. Comparison of HAADF STEM imaging (left) with elemental mappings (RGB on the right) extracted from STEM-EDX experiments. Different metals can be clearly distinguished.

Sample courtesy of P. Hozak, Institute of Molecular Genetics, Prague, Czech Republic.

Nanoparticles catalysts

In fuel cell technology, platinum nanoparticles are used as catalysts for large scale applications. The catalytic efficiency of Pt can be increased by adding Au. Catalytic nanoparticles produced by coating Au particles with Pt(Fe) were investigated.

With conventional EDX technology (upper Au and Pt maps in **Figure 18**) there is only an indication that particles may consist of a Au core surrounded by Pt. The Tecnai Osiris S/TEM (lower maps), however, clearly reveals the core-shell structure with 3 times the pixel resolution and 60 times the speed.

Due to the high speed and sensitivity of ChemiSTEM Technology the core-shell structure of many nanoparticles can be observed in a single EDX experiment. The lower Pt concentration in the center of all particles, due to their core-shell structure, can be seen in **Figure 19**.



Figure 18. Upper Au and Pt 64x64 pixel maps were recorded in three hours with a Tecnai TF20 ST TEM equipped with a standard Si(Li) detector. The lower 200x200 pixel maps were acquired in three minutes using ChemiSTEM Technology with a Tecnai Osiris S/TEM.

Samples and TF20 data courtesy of C. Wang, V. Stamenkovic, N. Markovic, N.J. Zaluzec (Argonne National Laboratory). Tecnai Osiris S/TEM experiments by D.O. Klenov (Thermo Fisher Scientific) and N.J. Zaluzec (ANL).



Figure 19. Elemental maps of 300 x 300 pixels were acquired using 100 µsec dwell time/pixel, a beam current of 0.9 nA, and a total acquisition time of less than four minutes (226 sec).

Samples courtesy of C. Wang, V. Stamenkovic, N. Markovic (Argonne National Laboratory); Tecnai Osiris S/TEM experiments by D.O. Klenov (Thermo Fisher Scientific) and N.J. Zaluzec (ANL).

Thin film / multilayer structures: Quantifying light elements

The large increase in chemical sensitivity of ChemiSTEM Technology allows for improved high-accuracy quantification of elements, whether for mapping or line profile analysis. One traditional challenge for EDX quantification is to distinguish elements with strong peak overlaps, as is the case for Ti and N (Ti-L strongly overlaps with N-K). The maps in Figure 20 show a sample with Ti/TiN multilayers separating AI from SiO_a. In this case, using quantification, the Ti and TiN layers are easily differentiated. Despite the large pixel count of such a map, each pixel has a fully recorded, complete spectra with good statistics. This means that all elements can be quantified and displayed after the data is obtained. For example, it is possible to see that the non-uniformity in the Ti layer is caused by interdiffusion of the aluminum and titanium (see red arrows in Ti and Al map). This would clearly be more challenging to do with techniques such as EFTEM.



Figure 20. Thin film structure with Ti/TiN multilayers separating SiO₂ from Al. Map parameters: 400x400 pixels, 50 µsec/pixel dwell time, multiple frames, 11 min total acquisition time, beam current 2.3 nA. There is X-ray spectra statistics for full quantification without binning.

Sample courtesy of IME, Singapore.

Figure 21. Line profile of the Ti/TiN multilayer with 0.5 sec dwell time per point and 1.5 nA beam current. Quantified profile shows that that the oxygen distribution in the area of Ti and Al interdiffusion is non-zero. Even for oxygen concentrations near 1%, this effect is still seen, despite the heavy peak overlap of Ti, N and O shown in the spectra (taken from the point marked by the cross). Despite the fact that light elements are considered the strength of ELS and usually a challenge for EDX, in this case, EELS struggles to quantify the same oxygen concentration due to the complexity of background subtraction.

Sample courtesy of IME, Singapore.



Compound semiconductor / quantum wells

InGaN quantum wells are widely used in light emitting devices, and the composition of the wells (in particular the indium (In) concentration) controls the frequency of the emitted light. Traditionally, the TEM could provide information about the geometry and atomic structure of the layers; however, the In concentrations were always difficult to measure due to the high sensitivity of the material to electron damage. The shorter required pixel dwell time of ChemiSTEM Technology, however, permits data acquisition for In. Nominal composition of In in the alternating layers was approximately 10%, 18% and 26%, with two sets of layers having this nominal composition.



Figure 22. EDX lineprofile across all layers with full quantification performed. 1,000 points, 0.5 sec dwell time, 0.25 nA beam current. The differences in composition between different layers are clearly quantifiable.



Figure 23. Fast ChemiSTEM Technology mapping was used to show the elemental distribution around a surface defect in less than five minutes. Map size 525x230 pixels, 50 µsec dwell time, multiple frames (iterative mapping), 276 sec total acquisition time, 1.7 nA beam current. Integrated intensities were used to show elemental distribution.

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ChemiSTEM Technology is available on many Thermo Scientific TEM platforms.

Main EDX-related specifications

- X-FEG Brightness
 - 1.8 x 10⁹ A/cm²/sr (@200 kV)
- X-FEG probe current
 - 0.4 nA in 0.31 nm spot (@200 kV)
 - 1.5 nA in 1 nm spot (@200 kV)
- Fast mapping: dwell time/pixel down to 10 μs
- Output count rate: up to 200 kcps

- Solid angle: 0.9 sr (Talos TEM); 0.7 sr (Themis S/TEM)
- Energy resolution
 - <136 eV @ Mn-K_a and 10 kcps (output)
 - <140 eV @ Mn-K_a and 100 kcps (output)
- High P/B ratio (Fiori number): >4,000
- Excellent EDX in-hole performance
 - <1% hole counts
 - Low system background in EDX
 - <1% spurious peaks</p>







For more information, visit thermofisher.com/TEM to download the product data sheets for our TEMs.



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