Nanoscale Chemical Compositional Analysis with an Innovative S/TEM-EDX System

Peter Schlossmacher, Dmitri O. Klenov, Bert Freitag, Sebastian von Harrach and Andy Steinbach
FEI Company, Eindhoven, The Netherlands

BIOGRAPHY

Peter Schlossmacher studied physics at the University of Cologne, Germany, with an emphasis on solid state physics. In his PhD thesis at the Research Center Jülich he investigated crystal defects in GaAs. Subsequently he moved to the Institute of Materials Research at the Research Center in Karlsruhe, Germany, as staff scientist where he headed the TEM laboratory. For the last 8 years he has worked for electron microscopy manufacturers and is currently Product Marketing Manager in the NanoResearch Market Division at FEI Company, responsible for TEM products with special focus on the Tecnai platform.

ABSTRACT

A new technology for energy dispersive X-ray spectroscopy (EDX) in the scanning/transmission electron microscope (S/TEM) is described that allows orders-of-magnitude improvement in key analytical metrics, such as sensitivity and time-to-data. This technology incorporates a four SDD detector system highly optimized for light element detection, collection efficiency, and improved tilt response. We believe this new technology will enable the S/TEM to answer many scientific and engineering questions that were previously out of reach and will lead to a renaissance of interest in using EDX as a prime tool in S/TEM microscopy and analytics. Here we describe the characteristics of the new EDX technology and illustrate its performance for the chemical analysis of several application challenges each requiring sensitivity and speed previously unattainable.

KEYWORDS

scanning transmission electron microscopy, energy-dispersive X-ray microanalysis, ChemiSTEM, Super-X, silicon drift detector, nanostructures

AUTHOR DETAILS

Peter Schlossmacher,
FEI Company,
Achtseweg Noord 5,
5600 KA Eindhoven, The Netherlands
Email: peter.schlossmacher@fei.com

Microscopy and Analysis 24(7):S5-S8 (AM), 2010

INTRODUCTION

ChemiSTEM Technology: A Revolutionary Advance in X-ray Analytics

Information about a material's chemical composition on the nanoscale is pivotal for an understanding of nanostructures and devices, and X-ray spectroscopy is a well-established, robust and easy-to-use technique to obtain this information. Better yet, the scanning/transmission electron microscope (S/TEM) can pair microstructural information obtained from high-resolution imaging with accurate chemical composition information. But there has been an historical limitation with X-ray systems for the S/TEM: they collect only about 1% or less of all X-rays generated by the electron beam passing through the very thin sample. Recently, as the desired spatial resolution of chemical analysis has become progressively greater, the X-ray signal has decreased due to fewer atoms excited in smaller analytical volumes (a consequence of smaller electron beams and thinner samples). This results in low signal strength, bringing about low sensitivity and hence long analysis times – until now.

ChemiSTEM™ technology has been developed at FEI over a 5-year period with the express purpose of removing the old barriers in performance, bringing orders-of-magnitude improvement in many key analytical 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 based on this new capability to answer scientific questions that have until today remained unanswered. We begin with an explanation of how this new proprietary technology is able to provide such breakthrough capabilities.

A key performance metric of energy-dispersive X-ray spectroscopy (EDX) is the net measured X-ray count rate which depends on the count generation rate (set by the beam current) and the collection efficiency (set by the detector system). The ChemiSTEM system design is shown in Figure 1; it addresses both needs: more beam current and more collection efficiency of X-rays. The higher beam current is provided by the proprietary X-FEG Schottky electron source. This FEI high-brightness electron source can generate up to 5 times more beam current at a given spatial resolution compared to a conventional Schottky FEG source. The higher efficiency detection system [1,2] is a radically new design concept: it integrates four FEI-designed silicon drift detectors (SDDs) 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 Super-X™ system.

Figure 2 shows the results of an analysis time benchmark test: The Tecnai Osiris 200 kV S/TEM (with ChemiSTEM technology) [3] was compared to a conventional 200 kV S/TEM using 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 for measurements on both systems. For equivalent EDX map sizes and statistics, the results took just under 2 hours on the conventional system and just under 2 minutes on the ChemiSTEM system, in other words from 'hours to minutes'. This demonstrates the magnitude of the new technology's performance advantage, that can be used as a raw speed advantage, but, perhaps more significantly, can be used to obtain results that were previously unobtainable, such as detection of 0.02 wt.% elemental concentrations, identification of a catalyst core-shell structure in 4 minutes, and fully quantified 600×600 pixel elemental maps in about an hour with a pixel resolution of 3 Å and yielding never-before-seen levels of light element detection such as C, O, and N. These examples are shown later in this article, but first we give a more detailed description of the benefits and advantages of the new technology.

The Super-X Advantage in Tilt Response

A major advantage of the Super-X design comes from the large solid angle for X-ray collection provided by four SDD detectors symmetrically arranged around the specimen. But there is also an important advantage related to specimen tilting. 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 were measured at 200

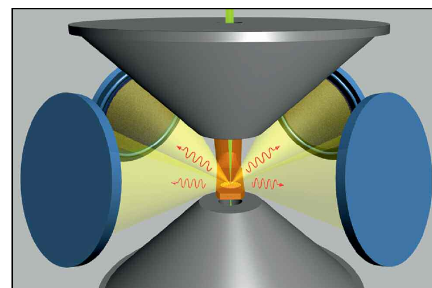


Figure 1:
A schematic of the ChemiSTEM™ design, showing the X-FEG high-brightness, Schottky electron source, and the Super-X™ geometry including four silicon drift detectors arranged symmetrically around the sample and the objective lens pole pieces. This schematic is not to scale.

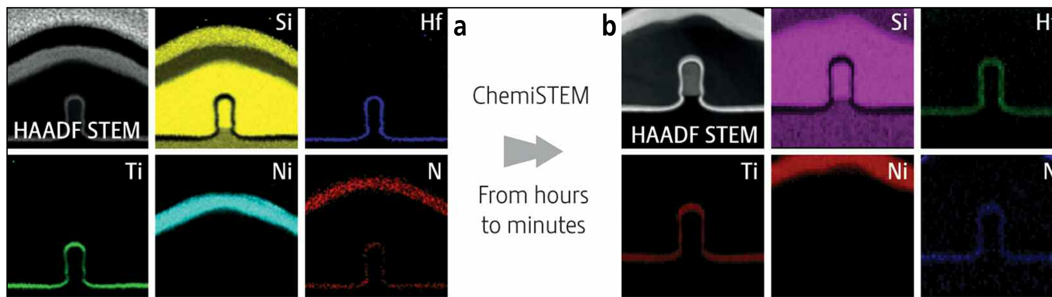


Figure 2: (a) 100x100 pixel EDX maps of a semiconductor device taken on a Tecnai TF20 XT (0.3 sr Si(Li) system) with 500 ms pixel^{-1} dwell times, ~0.7 nm spot size, 0.4 nA beam current, and 1h 54min total map acquisition time. Sample courtesy of NXP Research; maps by D. Klenov, A. Carlsson, FEI. (b) 100x100 pixel EDX maps of an equivalent semiconductor taken on a Tecnai Osiris with ChemiSTEM technology with 5 ms pixel^{-1} dwell times, ~0.3 nm spot size, 1.0 nA beam current, and 115s mapping time.

kV using standard commercially available NiOx test films [4] with nominal thicknesses of 50±10 nm and integrated over the entire energy range. The count rate is normalized to unity at the maximum response of the Super-X system, occurring at zero tilt angle. The Super-X 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, and it occurs equally for SDD or Si(Li) detectors.

The ability to achieve high X-ray signal over the whole 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 then does not need to be readjusted for optimum EDX analysis conditions. Conversely, for very many samples, an important crystal orientation to be observed is prepared to be very close to zero degrees tilt. For such samples, it is a key advantage to have the maximum X-ray response at zero tilt, as opposed to the ~30% reduction in response single detector systems experience due to detector shadowing at zero tilt. 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 of the interface).

Super-X Advantage in Total Response (1+1+1+1>4)

By simple logic, one expects the Super-X system with four detectors to be '4 times better' in response than a one detector system (i.e., 1+1+1+1 = 4). However, this logic does not hold, because each individual Super-X SDD detector has significant design improvements in and of itself, compared to conventional individual SDD detector systems. So the response of each Super-X detector is '> 1'. The question of how much greater leads us to consider two major design improvements of the individual detectors. First, as described earlier, since the individual Super-X SDD detectors were designed to be optimized for the FEI 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 each detector sits at a 'take-off' angle and location so that the detector is fully illuminated at zero tilt, with no shadowing loss. Achieving this required the design of a special sample holder for the Super-X system, as well as an optimized detector design.

Second, the Super-X detectors are windowless by design. The detectors instead have mechanical shutters providing complete protection when they are not in live mode. This choice eliminates the need for ultra-thin polymer windows that are the source of two severe response losses for systems that do employ them. Figure 4 illustrates the effect of windows on X-ray collection efficiency, and there are two key effects to understand, which are illustrated by the diagram in Figure 4a. First, the polymer film [5] is supported by a silicon support grid, which blocks all X-rays hitting it and 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, which plots X-ray transmission efficiency for an SDD detector both with and without polymer windows. This figure shows that the efficiency loss due to windows (lower blue curve) is significant over the entire energy range (due to the polymer support grid), 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 2-3 greater transmission efficiency at energies below 500 eV. This improvement in low energy X-ray transmission has a huge impact on light element detection, as we will discuss later.

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 the distance from the eucentric point. Problematically, this does not include signal loss from effects such as detector shadowing or windows, which make quite a difference, as we've seen. Sometimes non-active detector areas such as metallic guard rings will be included when calculating nominal solid angle. True efficiencies thus depend on loss factors based on often unknown parameters such as sample holder geometry or detector elevation angle, etc., and these parameters are not realistically obtainable by users. We propose that the most accurate way to compare EDX system efficiency is by a method that involves measuring actual X-ray count rates per applied beam current using a standard sample of known thickness.

We have applied this comparison methodology and the results are 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 with ChemiSTEM technology and a 200 kV S/TEM with Schottky FEG and Si(Li) detector of 0.3 sr nominal solid angle. The small inset shows the same data on a smaller scale closer to the origin. For both measure-

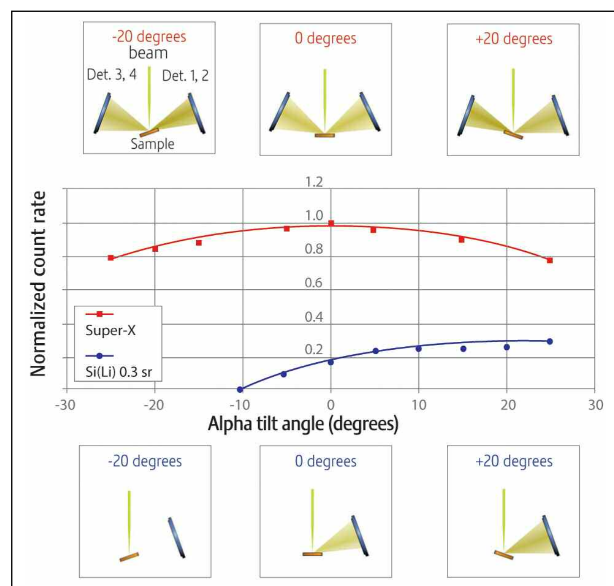


Figure 3: Comparison of relative EDX count rates of the Super-X system (on a Tecnai Osiris with 0.9 sr collection angle) and a single Si(Li) detector system with 0.3 sr nominal solid angle. Both S/TEMs were operated at 200 kV with the same (constant) beam current. NiOx films were used as samples for both tilt series. 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 detectors, and diagrams below show shadowing effects for the single detector system.

ments, 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 observation from this figure is that the ChemiSTEM system on the Tecnai Osiris achieves more than 5 times the X-ray count rate per unit applied beam current than the conventional system, even though this system is an 0.3 sr nominal solid angle EDX system, which is considered at the high end of collection performance for conventional detectors. In real experiments, we typically find a 5-10 times collection advantage of the Super-X system compared to single-detector systems. The second observation from Figure 5 is that more than 10 times higher beam currents can be applied for the ChemiSTEM system with the X-FEG electron gun, without high dead-time % saturation of the new Super-X detector system. At an applied beam current of 10 nA the input X-ray count rate is over 400,000 cps at approximately a 50% dead time of the Super-X detector system, meaning that the output X-ray count rate is over 200,000 cps at this value of 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, and thus 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. For example, in benchmark tests performed at 200,000 output cps the Super-X system achieved typical energy resolution of 136 eV (@ Mn Kα), whereas other single SDD systems showed typical energy resolutions of 160 eV (Mn Kα) or higher at the same count rate.

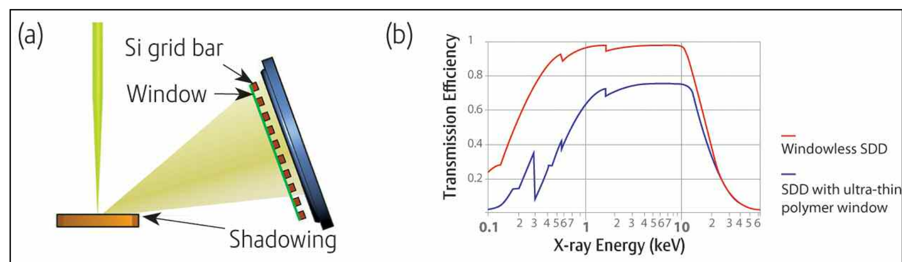


Figure 4:
(a) Schematic showing loss due to holder shadowing and detector window. Loss due to the window includes total absorption by the Si support grid bars (at all energies) and selective absorption by the polymer window (at energies below 1 keV). (b) X-ray transmission efficiency versus energy for 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.

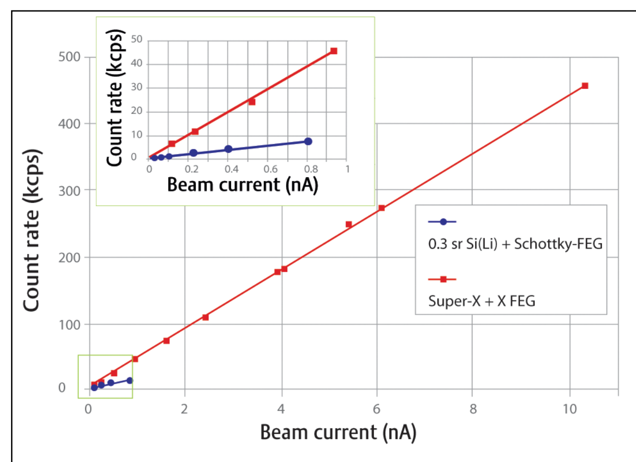
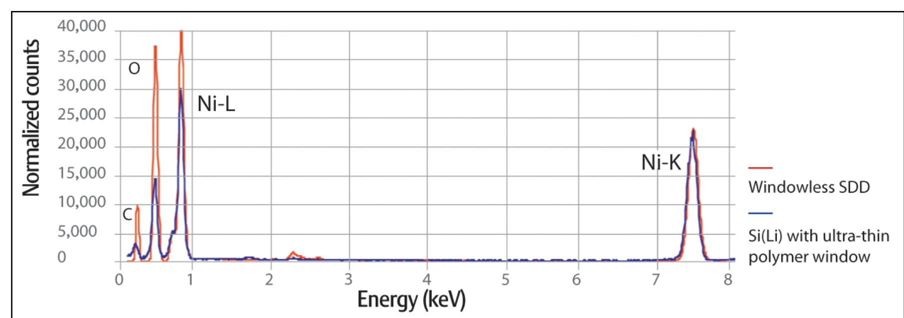


Figure 5 (left):
Input count rate for ChemiSTEM technology (red curve) compared to standard technology consisting of Schottky FEG and 0.3 sr Si(Li) detector (blue curve). For details see text.

Figure 6 (below):
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.



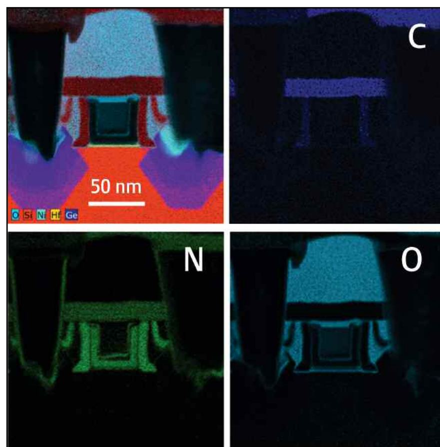
Light Element Sensitivity

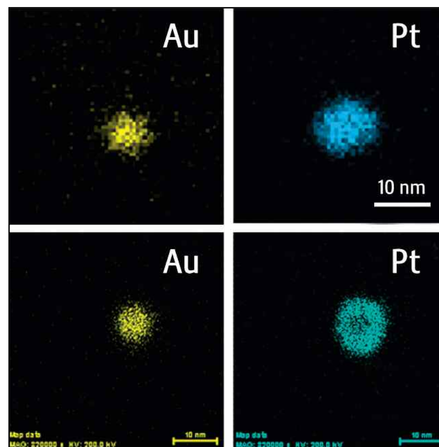
Poor detection of light elements (such as C, O, and N) has always been considered one of the big weaknesses of EDX as a technique, but ChemiSTEM technology removes this barrier to light element sensitivity. As shown in figure 4, the relative sensitivity of the windowless system for low energy X-rays in 500 eV or lower range is several times higher than systems with ultra-thin polymer windows. When this low-energy advantage is combined with the energy-independent five to ten times collection advantage of the Super-X system, it leads to an order-of-magnitude boost in light element detection performance.

In Figure 6 we show measured data to demonstrate that the enhanced low energy performance shown Figure 4 is realized in the Super-X system. The figure shows a spectra from a NiOx film measured on the windowless Super-X system and a conventional EDX system with ultra-thin polymer windows. The count rates of both spectra have been normalized (set equal) at the Ni-K line at 7.4 keV in order to demonstrate only the relative differences in low energy efficiency. One can then see the advantage of the windowless system by noting the higher counts in the 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 collection efficiency increase (which is energy independent) since this has been removed in Figure 6 by the normalization. Dramatic examples of the improved light element detection are found in the 45 nm PMOS example in the next section

ChemiSTEM Application Examples: Fast Mapping at High Sensitivities

Figure 7 shows a ChemiSTEM 600×600 pixel EDX map of a 45 nm PMOS transistor structure. Semiconductor devices represent a demanding application for chemical analysis because they contain both heavy elements like tungsten (W), hafnium (Hf), and tantalum (Ta), as well as light elements like nitrogen (N), oxygen (O), and sometimes even carbon (C), and measuring the accurate quantitative distribution of all these elements is necessary for device design and for monitoring process success and quality. With the increased sensitivity for light element detection, now virtually all element of the periodic system can be detected in one EDX map acquisition. The map spans a large field-of-view of about 190 nm and a pixel resolution of ~0.3 nm $pixel^{-1}$. This map data was acquired at a spectrum imaging rate of 20,000 spectra s^{-1} (50 μs $pixel^{-1}$ dwell time) and 1 nA beam current with drift correction applied to acquire multiple frames in 100 minutes. The short pixel dwell times of 50 μs were necessary in this case to avoid sample damage (such as changing the local distribution of carbon in the sample). The fast electronics of the Super-X system permits pixel dwell times as low as 10 μs (allowing spectral EDX rates of almost 100,000 spectra s^{-1}). The total acquisition time of 100 minutes was chosen to obtain good X-ray count statistics permitting full quantification of each pixel (without any binning). This high field-of-view, high spatial resolution, high statistics data set contains a huge amount of information and is only possible in a reasonable time due to the high sensitivity and high-brightness source of the ChemiSTEM system. We estimate that such a map would require more than three full days of mapping time on a conventional system, which is not practically possible to due instrument drift and practical throughput concerns. The nitrogen, oxygen, and carbon maps seen in





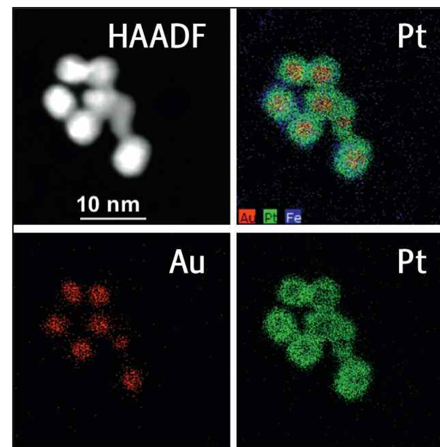


Figure 7:
600x600 pixel maps of a 45 nm PMOS transistor structure recorded with 50 μs pixel^{-1} dwell time and 1 nA beam current. Drift correction was applied to acquire multiple frames in 100 minutes. The maps were fully quantified to eliminate contributions from overlapping peaks. Data courtesy of D. Klenov, FEI.

Figure 8:
Upper Au and Pt maps were recorded with a Tecnai TF20ST equipped with a standard Si(Li) detector as 64x64 pixel maps in 3 hours. The lower maps were acquired using ChemiSTEM technology with a Tecnai Osiris: 200x200 pixel maps in 3 minutes. Samples and TF20 data courtesy of C. Wang, V. Stamenkovic, N. Markovic, N. Zaluzec (Argonne National Laboratory). Tecnai Osiris experiments by D. Klenov (FEI) and N. Zaluzec.

Figure 9:
Elemental maps at 300 x 300 pixels were acquired using 100 μs dwell time per pixel, a beam current of 0.9 nA, and a total acquisition time of less than 4 minutes (226 sec). Samples courtesy of C. Wang, V. Stamenkovic, N. Markovic (Argonne National Laboratory). Tecnai Osiris experiments by D. Klenov (FEI) and N. J. Zaluzec (ANL).

Figure 7 show that fast mapping of light elements is possible in reasonable times, which really represents a breakthrough in capability for the technique of analytical S/TEM-EDX. Additional elemental maps from this same sample are shown on the cover of this Nanotechnology Supplement.

In fuel cell technology Pt nanoparticles are used as catalysts for large scale applications. The catalytic efficiency and stability of Pt can be increased by adding Au and Fe to the nanoparticles. Such nanoparticles produced by coating Au particles with Pt(Fe) were investigated, and a key materials composition question is: Do the particles form a core-shell structure or not? With conventional EDX technology (upper Au and Pt maps in Figure 8) there is only an indication that particles may consist of a Au core surrounded by Pt. Tecnai Osiris (lower maps) however clearly reveals the core-shell structure with three times better pixel resolution and 60 times faster. Due to the high speed and sensitivity of ChemiSTEM technology the core-shell structure of many nanoparticles can be observed in a single, fast EDX experiment, as shown in Figure 9. The lower Pt concentration in the center of all particles due to their core shell structure can be clearly seen, as well as the presence of Fe in low concentrations, also distributed in a shell geometry (the blue color in the composite map in Figure 9).

Ultimate Sensitivity: The 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 the improved performance can also be used to achieve much higher sensitivities than were previously possible. This benefit is ultimately perhaps more important than speed, because it allows the detection of hidden features and elements that previously could not be seen. The ultimate test of EDX raw sensitivity is the ability to detect very low concentrations of elements, for example, well below 1 wt.%.

In Figure 10 we show the results of an experiment demonstrating the sensitivity limits of ChemiSTEM technology. This figure 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 an FIB, it is expected that minimal changes have resulted in the composition. The full spectrum in Figure 10 was acquired in 600 seconds using a beam current of 1.7 nA while scanning a micron-sized area in order to average the composition over the microstructure of the steel.

The three smaller zoomed spectra at the bottom of Figure 10 show clear peaks from these 3 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 Tecnai Osiris is capable of detecting low concentrations such as the ~0.02 wt.% concentrations in this certified NIST steel sample, obtained in a reasonable 10 minutes total acquisition time.

CONCLUSIONS

Whether the application calls for using the ultimate speed benefits of ChemiSTEM technology (mapping in 'hours to minutes', or huge area maps with unprecedented sensitivity in reasonable times), or the pursuit of ultimate sensitivity (pushing to detection of ultra-low concentrations or hidden sample features) we believe ChemiSTEM will give the scientific community the capability to answer many questions that were until now unresolved and will lead to a renaissance of interest in using EDX technology as a prime tool in S/TEM microscopy and analytics.

REFERENCES

1. von Harrach, H. S. et al. Microscopy and Microanalysis 15 (Suppl 2):208, 2009.
2. von Harrach, H. S. et al. Proceedings of EMAG 2009.
3. www.fei.com/products/transmission-electron-microscopes/tecnai.aspx
4. Commercially available from Agar or Pelco based on R. F. Egerten and S. C. Cheng. Ultramicroscopy 55:43, 1994.
5. www.moxtek.com/x-ray-windows/ap3-ultra-thin-polymer-windows.html2.

©2010 John Wiley & Sons, Ltd

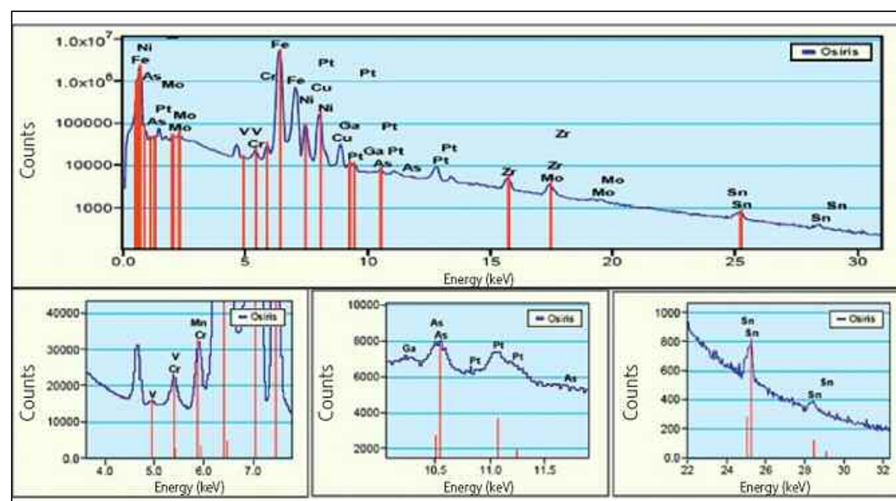


Figure 10:
Top: Super-X spectrum of NIST steel standard NBS No.461 (log scale). Bottom: Zoomed spectra showing minor elements of vanadium (0.024 wt.%), arsenic (0.028 wt.%) and tin (0.022 wt.%). Ga and Pt peaks are due to FIB preparation.