### ABSTRACT

We describe the development of a new tomography technique for scanning transmission electron microscopy (STEM) coupled with X-ray energy dispersive spectrometry (XEDS) which provides the 3D distribution of elements at the nanometer scale. This technique utilizes combination of a four silicon drift detector system and a high brightness electron gun optimized for high X-ray collection efficiency, fast XEDS mapping and improved tilt response. To assess the merits of this new technique, a series of 2D maps of various elements were acquired for a range of tilt angles and reconstructed to obtain the 3D distribution of elements in materials with a complex microstructure and architecture. We present this new technique as a fast and practical way of conducting 3D chemical analysis in the TEM by employing conventionally prepared FIB lamellas and high speed XEDS mapping.

### KEYWORDS

scanning transmission electron microscopy, energy dispersive X-ray spectrometry, tomography, chemical mapping, focused ion beam, silicon drift detectors, superalloys

### INTRODUCTION

There is a constant demand in research and industry to obtain more information from increasingly smaller features using transmission electron microscopy (TEM) techniques. This leads to the situation where two-dimensional projections are no longer sufficient for full specimen characterization when the features of interest are considerably smaller than the TEM foil thicknesses. To overcome this problem, electron microscopists in materials science have been utilizing computed tomography techniques.

Most electron tomography in materials science has been performed using bright field (BF) TEM or high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) based techniques. Since HAADF STEM technique has a monotonic signal increase with sample thickness, it fulfills more closely the projection requirement for tomographic reconstruction than brightness-STEM, which usually contains the effects of diffraction contrast and does not match this requirement. Both techniques do not provide direct 3D chemical information.

Three-dimensional composition mapping using energy-filtered TEM (EFTEM) [1], electron-energy-loss spectrometry (EELS) [2] and X-ray energy-dispersive spectrometry (XEDS) [3] combined with tilt tomography have also been pursued. EFTEM tomography has a clear practical advantage due to the necessity of acquiring many images in a tomographic tilt series. EFTEM elemental maps can be acquired typically in less than one minute from a large specimen area while XEDS spectrum images require much longer acquisition times making the many hours for tilt-series acquisition prohibitive, assuming the specimen can withstand the high electron doses typically used. Nevertheless elemental imaging with EFTEM suffers from background artifacts due to the relative high background signal in EELS. This problem of high background signal increases when lamella samples are studied, because the thickness increases by a factor of 3 when tilting to 70° causing a background increase of one to two magnitudes.

XEDS tomography using traditional single detector designs based on Si(Li) or SDD detectors suffers from the additional problem that the specimen or stage will ‘shadow’ the single detector and the number of X-rays detected will vary significantly with specimen tilt. To avoid this problem, previous researchers have used a rod-shaped specimen prepared by a focused-ion beam (FIB) instrument and mounted in a specially designed tomography holder [2-4]. Unfortunately, this also limits the field of view that can be analyzed in the specimen. On the other hand, XEDS spectrum imaging has a clear advantage over EFTEM or EELS spectrum imaging in that a large number of elements can be simultaneously mapped and a full spectrum containing peaks from nearly all elements of interest is available at each pixel for post-acquisition analysis. In addition, many elements of interest have poor EELS edge jump ratios for mapping making EFTEM or EELS tomography difficult or impossible, especially when relatively thick TEM foils are used [5,6].

Here we describe the application of a new chemical mapping method (ChemiSTEM Technology, FEI Company, Hillsboro, OR, USA) which resolves many of the current problems of XEDS tomography and enables the acquisition of three-dimensional chemical maps of many different elements.

![Figure 1](image.png)

(a) Comparison of relative XEDS count rates of Supra-X four detector system versus a single detector system. Data courtesy of P. Schlossmacher (FEI Company) [7]. (b) Variation in X-ray peak to background (P/B) ratio in XEDS as a function of A. (A = mean free path) XEDS data courtesy of Dr. Nestor J. Zaluzec, Argonne National Laboratory, USA [5].

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### BIOGRAPHY

Arda Genç received his PhD in materials science and engineering from Ohio State University under the guidance of Dr. Hamish L. Fraser and subsequently worked as a post-doctorate associate at the Center for Accelerated Maturation of Materials at Ohio State University. In 2008, he joined Portland Technology Development at Intel Corporation as a Failure Analysis Engineer and worked on TEM characterization of planar and non-planar semiconductor devices. He is now a Senior Research Scientist at FEI focused on TEM applications and an on-site assignee for TEM applications support at the Pacific Northwest National Laboratory in Richland, WA, USA.

### REFERENCES

CHEMICAL MAPPING STEM TECHNOLOGY

For decades, XEDS in the TEM has been a technique limited by the poor collection efficiency of Si(Li) detectors. Most conventional detectors have a limited solid-angle (Ω) of ~0.1 sr and additional absorption of light element signals due to polymer windows. Despite this very poor collection, XEDS detectors are very common in modern instruments due to the ease of obtaining elemental information from small volumes, often with less complexity than EELS.

A new XEDS system (SuperX, FEI Company) is a significant leap forward in XEDS analysis because of its high solid-angle of detection (Ω = 0.9 sr) and windowless design [7]. This is achieved by using four silicon-drift detectors (SDDs) placed around the specimen in a specially designed objective lens, while still maintaining excellent STEM and TEM spatial resolution. A brand of chemical mapping technology (ChemSTEM, FEI Company) combines the SuperX X-ray detector configuration with a high-brightness gun (X-FEG, FEI Company). This combination provides enhanced generation of X-rays and together with high detector efficiency results in a faster mapping of larger areas in XEDS spectrum images (SIs) [7]. The improvement in signal is roughly a factor of 50 leading to minutes of acquisition for mapping instead of hours in the past.

In this work, SIs are obtained by summing multiple frames where each frame is obtained with very short dwell times (typically on the order of tens of microseconds) per pixel, which is a new feature for XEDS mapping in STEM. This helps to reduce specimen damage as the beam is not parked on any specimen region for a long period of time. The fast mapping capability makes it possible to obtain composition maps in much shorter time periods from large specimen areas and reduces the total time needed for a tomography tilt series.

The use of the enhanced XEDS system also avoids the detection problems related to specimen tilting, because the X-ray detection has a minimum dependence on the specimen tilt [7]. As shown in the graph in Figure 1a, the symmetry axis of the detector not only allows for optimum collection angle at 0° tilt, but also provides sufficient XEDS signal under all tilt conditions [7]. This feature makes the complicated preparation of rod-shaped specimens obsolete for 3D XEDS studies. Standard 3 mm disk specimens or FIB lamella used in routine TEM analysis can easily be used for XEDS tomography in the enhanced XEDS system. This configuration also permits mapping at the high tilt angles normally used in HAADF-STEM or EFTEM tomography experiments. High tilt angles are critical for good resolution in the tomography reconstruction.

Additionally, the high speed data processing of the four detector system allows for extreme high output count rates (~200 kcps), which is required to acquire XEDS maps of thick samples and high tilt angles in 3D tomography. The XEDS signal increases monotonically similar to the HAADF STEM signal with the mass thickness of the material as comparison of experimental data with theoretical calculations shows [8]. In contrast to the EELS, the peak to background ratio (P/B) of the XEDS signal does not change, even with a thickness increase by a factor of 3, as shown in Figure 1b [5]. Here the P/B ratio of low atomic number elements like oxygen increases only by a factor of two, while higher energy peaks (e.g. Ni L-edge, Ni K-edge) show even only a change of 5-10%. This kind of increase is typical in a 3D tomographic series of lamella samples, when tilting the TEM sample in the range of 0° to 70° and the constant P/B ratio allows for an easy reconstruction of the 3D XEDS data compared to the EELS data.

APPLICATIONS OF STEM XEDS 3D TOMOGRAPHY

TEM foils used in tomography experiments were prepared as a thin lamella using the conventional lift-out FIB technique. Data acquisition consisted of an automated STEM tomography procedure using Explore 3D (FEI) software and acquisition of STEM-EDS SIs using the Espirit software (Bruker). Each 512 x 512 pixel SI was acquired for 8 minutes and total acquisition time was ~4 hours for a tilt series from -45° to +50° in 5° increments (a 32-nm silicon device) and each 1024×1024 pixel for 5 minutes and total acquisition time of ~6 hours for a tilt series from -48° to +57° in 3° increments (Ni-based superalloy). Elemental maps were acquired using an FEI Tecnai Osiris S/TEM microscope operated at beam current of 1.5 nA with a 1 nm probe size and accelerating voltage of 200 kV. Data processing was done by using Inspect3D software (FEI) with the simultaneous iterative reconstruction technique (SIRT) algorithm followed by segmentation of the 3D dataset using Resolve RT/Amira.

Figure 2 shows an example of 3D tomography applied to a Ni-based superalloy using both HAADF STEM and STEM XEDS techniques. Complex Ni-based superalloys are of great interest for high temperature and high stress applications in the aerospace industry. The unique mechanical properties of Ni-based superalloys are often optimized by tailoring the microstructure of the material through the addition of various alloying elements and it is critical to understand how these alloying elements are partitioned between matrix (γ) and precipitate (γ') phases. For example, addition
of alloying elements like Al, Co, Cr and Re modifies the γ/γ’ microstructure and grain boundary morphology and improves the creep properties of the superalloy.

Figure 2 compares the γ/γ’ microstructure of Ni-based superalloy as revealed via HAADF STEM and STEM XEDS 3D tomography (upper half) and conventional 2D elemental mapping (lower half) of Ni (K-edge) as well as Al (K-edge), Co (K-edge), Cr (K-edge) and Re (L-edge). As seen in Figure 2, STEM XEDS 3D tomography simply resolves the true structure of material and reveals the distribution of individual elements through the thickness of the TEM foil. This comparison also depicts the superior chemical sensitivity of STEM XEDS tomography over conventional HAADF STEM tomography in a multi-component system.

Figure 3 shows a series of titanium (Ti) elemental maps acquired from a 32-nm Si device at different specimen tilt angles and region of interest where the mapping has been employed in the FIB-prepared TEM foil. The individual spectra were background subtracted so the maps show the integrated intensity for the Ti K-edge. No other post-acquisition process, such as any principle component analysis (PCA), has been applied to this tilt series data. It is worthwhile to note that for a single XEDS detector, spectrum imaging at negative tilt angles would be difficult or impossible due to the low count rates. The Ti elemental map tilt series show Ti within the metal contacts and metal gate region in the tilt range of -45° to +50°.

Figure 4a is a 3D representation of the metal contact region. Critical device properties and failure mechanisms in a planar transistor, such as contact resistivity and contact to gate shortage, are strongly controlled by the chemistry and morphology of metal components in this region. For instance, total surface area and volume of nickel-salicide and its 3D morphology within the contact region can easily be determined by the 3D analysis of nickel elemental distribution.

Figure 4b shows the complete tomography reconstruction of a total of nine elements in the 32-nm silicon device. Overlape between elemental maps were resolved by fitting the data to Gaussians using known peak-height ratios in the spectrum images prior to tomography reconstruction. It is clear from this image that within a few hours of acquisition time it is possible to gather 3D chemical information of nine different elements from a silicon-based device.

**CONCLUSIONS**

A new technique in 3D chemical analysis of materials using STEM XEDS is presented. The combination of a high-brightness electron gun with four SDDs and a large XEDS collection angle enables the relatively rapid acquisition of XEDS tomograms while avoiding some of the limitations associated with using a single detector system. In particular, this new technique permits a larger field of view due to the higher X-ray counts and reduces the acquisition time of a complete XEDS mapping tilt series to hours instead of days, which were impractical before. The benefits of the high P/B ratio and its insignificant change with sample thickness in XEDS permits the use of conventionally prepared FIB foils for 3D chemical mapping and overcomes the difficulties related to background changes with thickness increase known in EELS. XEDS gives access to all elements in the periodic table with higher atomic number than lithium for this type of application. We believe that this new technique will facilitate the applications of STEM coupled with XEDS tomography in 3D chemical analysis of materials and introduce a new dimension to the researchers and engineers in analytical characterization of thin TEM foils.

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**REFERENCES**


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