Phase Identification and Mapping Based on Valence Loss EELS and ELNES

R.D. Twesten
Gatan, Inc., Pleasanton, CA
rtwesten@gatan.com

Much of analytical TEM is based on elemental analysis of core-shell ionizations and their role in electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS). In these techniques, integrals of the primary or secondary ionization signals (typically over many tens of eV in energy) are used to measure and map the elemental composition of probed sample areas.

In contrast, present-day STEM EELS systems are able to reveal spectral details with resolution in the range 0.1-1.0 eV. This means that EELS provides access to electronic structure and response information that goes beyond the simple elemental composition information of the integrated core-loss signals. Such high-resolution electronic information is expressed in EELS spectra taken from the 0-30 eV low-loss range (valence loss EELS or VEELS) and in fine structure within a similar energy range of core ionization edge thresholds (energy-loss near-edge structure or ELNES).

Modern EELS spectrometers provides direct access to this type of specimen information (when mounted to a TEM/STEM instrument with a beam source of comparable energy resolution). With the addition of advanced STEM mapping software, you can explore variations in the EELS fine structure in different sample areas in real time. By systematically accumulating collections of such EELS spectra into spectrum image (SI) data sets and applying the analysis tools used by EELS Analysis software, you can begin to form maps of different material phases based on differences in VEELS and ELNES.

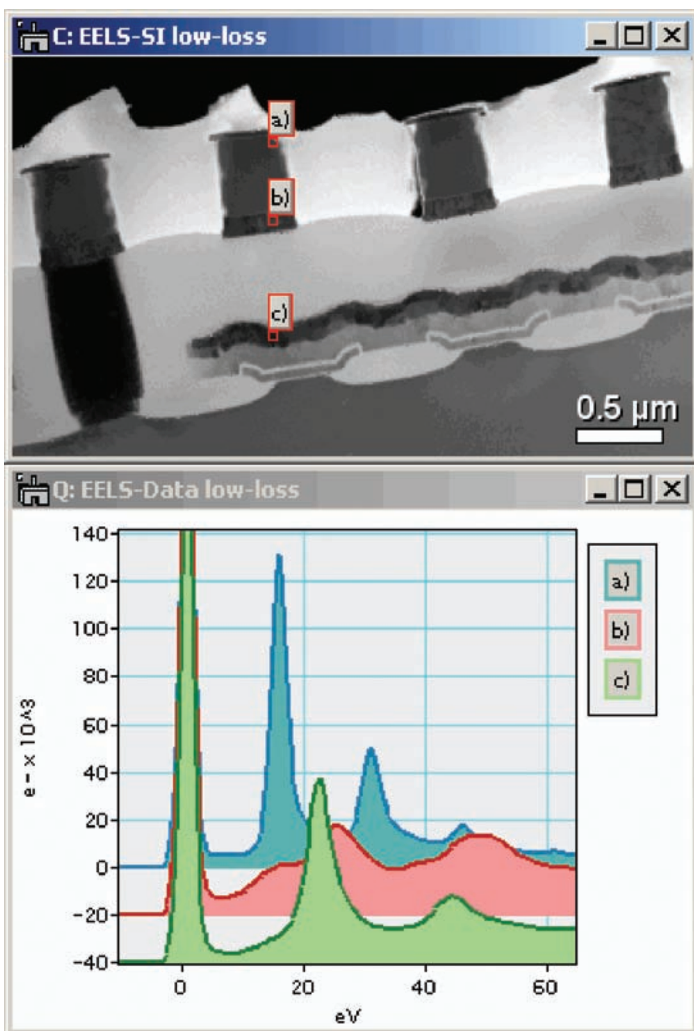


Figure 1 EELS data set being explored, post-acquisition, with the Spectrum Picker tool of the Gatan Microscopy Suite (GMS ®) software. Three representative areas (points a-c) extracted from the full 330 x 190 spectra in the data set.

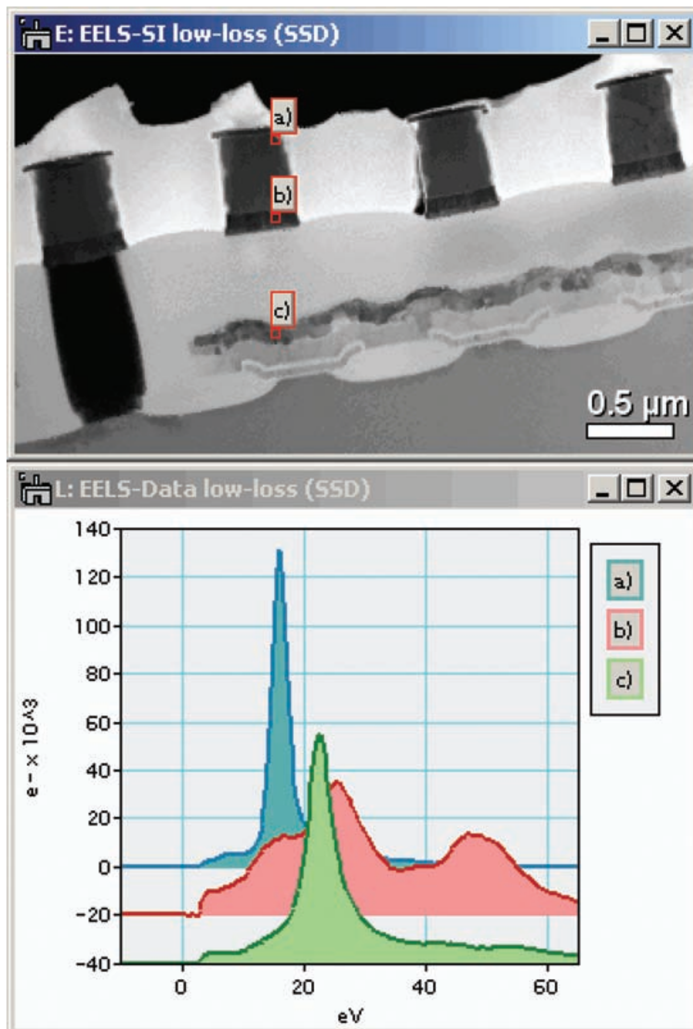


Figure 2 Data from Figure 1 after single scattering deconvolution.

Valence-loss EELS mapping

A key requirement of a VEELS detector system is its ability to capture EELS spectra with short exposure times and at high readout rates. This means even low-loss spectra with intense zero-loss peaks can easily be viewed in real time and rapidly collected into complete and detailed spectrum-image data sets. For example the movie (download at: http://www.gatan.com/resources/answers/2.php) shows such a data set being explored, post-acquisition, with the "Spectrum Picker" tool of the Gatan Microscopy Suite (GMS)® software.

https://doi.org/10.1017/S1551929500050069 Published online by Cambridge University Press

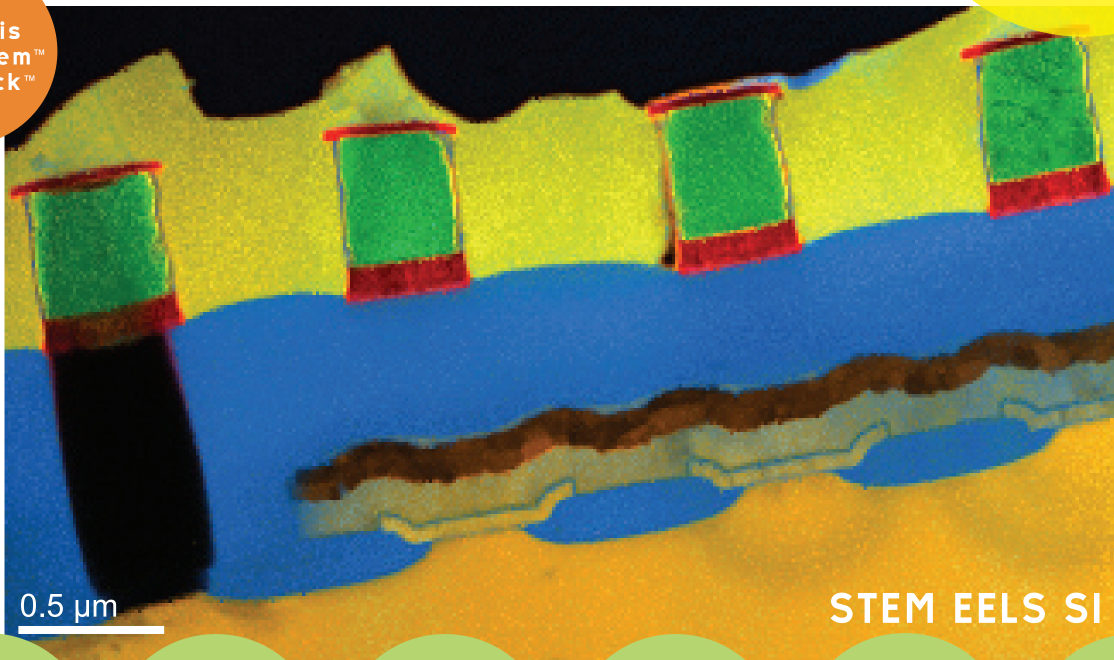
gatan gets it

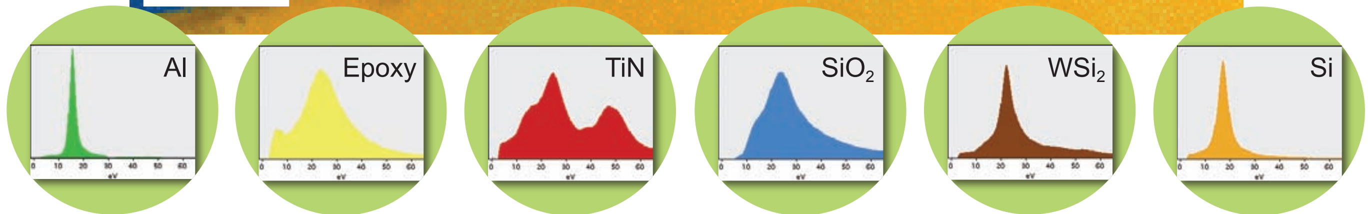
Can your **analytical TEM** system distinguish and map chemical phases based on electronic structure and response?

To learn how our EELS analysis tools accomplish this, visit us at www.gatan.com/answers

Chemical phase identification and mapping in a semiconductor device

EELS Analysis GIF Tridiem™ STEMPack™





https://doi.org/10.1017/S1551929500050069 Published online by Cambridge University Press

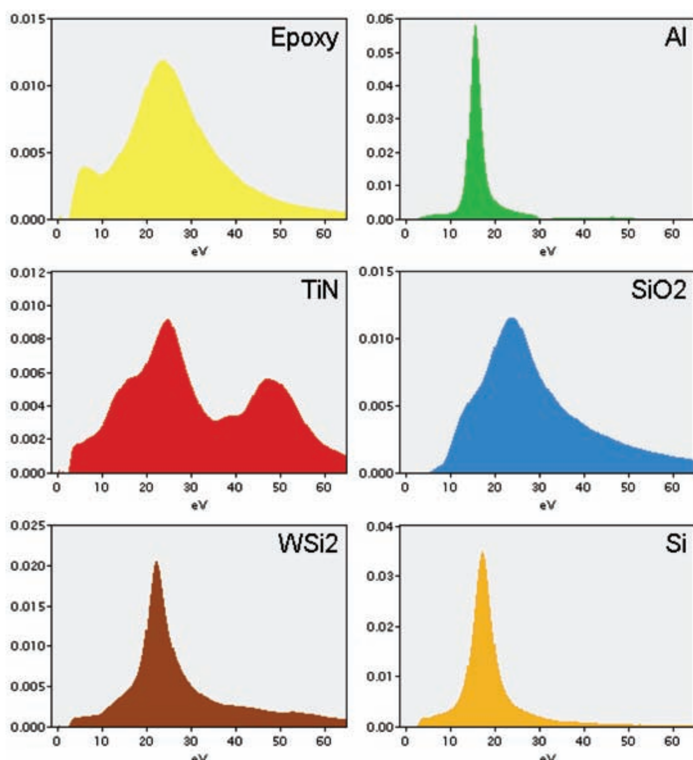


Figure 3, VEELS derived reference SSD spectra

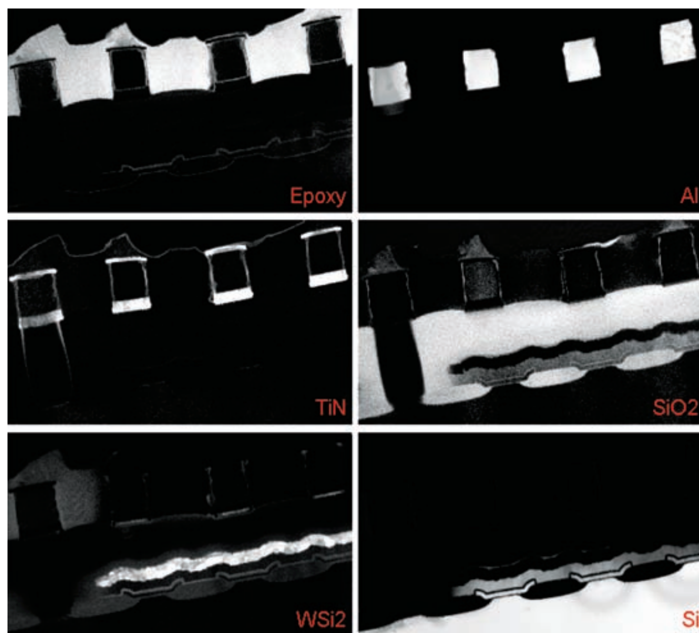


Figure 4, Element distribution maps created from the full SSD data set utilizing the reference spectra seen in figure 3.

Note that this spectrum image data set is unusual for its high degree of spatial information. In fact, it represents a scan of 330 × 190 pixels. Such image detail in STEM SI data becomes a practical possibility for EELS systems with high spectral readout rates. The scan shown in figure 1 was taken with an exposure time of 5 msec per pixel. At a readout rate of 40 spectra per second, the total acquisition time is less than half an hour.

By observing the spectra while scanning the probe around the sample, it becomes clear that each phase has distinct details in the valence-loss range. For example, compare the point labeled a-c in figure 1. In some cases, the chief difference lies in the position or width of the plasmon peak. In other cases, it is in the presence or absence of interband transitions below the plasmon peak. In addition to the inherent differences in the VEELS fine structure, the data in figure 1 unfortunately also reflects variations that are purely related to multiple scattering and variations in effective specimen thickness. These confounding effects hinder the isolation of unique characteristic signals that might be harnessed for chemical phase mapping.

The EELS Analysis tools of the GMS® software allow the multiple-scattering limitation to be overcome. The Fourier-log deconvolution function can be applied to entire STEM EELS SI data sets, thereby extracting the single-scattering distribution (SSD) at each pixel. Doing so with the data yields the EELS SSD SI shown in figure 2 and the supplemental movie data.

MLLS Fitting – generating phase maps from processed STEM EELS data

The shape of the SSD of each material in this particular semiconductor device sample is evidently fairly unique and characteristic of that particular phase. The characteristic SSD profile is stable against thickness variations and thus can form the basis of a signal extraction and mapping approach based on multiple linear least squares (MLLS) fitting to reference spectra.

Taking VEELS spectra from representative sample areas of known composition, performing Fourier-log deconvolution on each one, and normalizing the result yields the reference SSD spectra seen in figure 3. Using these and the full STEM EELS SI data set above as inputs to the MLLS fitting routine in GMS® yields the following maps of the fit coefficient values, figure 4.

The above maps illustrate both the strengths and weaknesses of the MLLS approach for this type of phase mapping. Overall, the images above give very good separation of the different phases. This is largely because of the clear differences between the reference spectra, i.e. there is a large degree of orthogonality between the various SSDs. These distinct differences make it possible for the MLLS routine to identify some sample areas where two of the phases (e.g. Si and SiO_2) appear to overlap through the thickness of this ion-milled sample. On the other hand, there are clearly areas, especially near interfaces, where artifact contrast appears (e.g. in the epoxy map) because the mixture of two different SSD signals can sometimes closely resemble that of a single non-related material. This demonstrates a key weakness of the MLLS approach, i.e. that it only works well when the reference spectra are truly linearly independent. In complex situations with many phases, there is a good chance that several references will have a good deal of commonality and so cannot be distinguished via the simple MLLS approach. A further weakness is that the MLLS approach is only as good as the reference spectra it is given. If no reference spectrum is provided for an important component of the sample, then that sample area is very likely to show up as artifact contrast in several of the maps generated.

After some further processing of the MLLS fit coefficient maps to reduce artifact contrast and noise, application of the

https://doi.org/10.1017/S1551929500050069 Published online by Cambridge University Press

Color Mix tool within GMS ® yields the informative map of the major phases in this sample. This mapping is show in figure 5 where the phases had been recombined into a single image using the color scheme from figure 3. ■

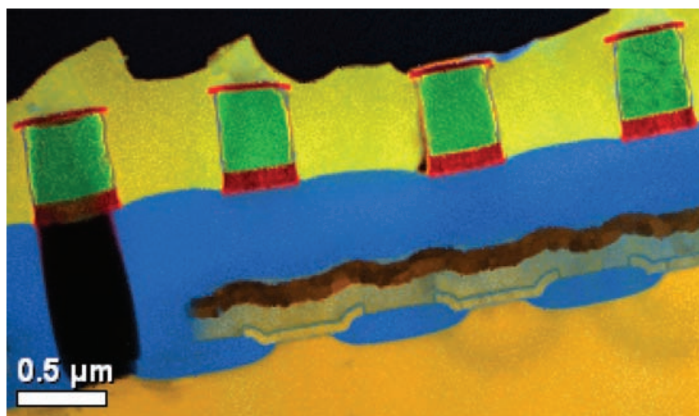


Figure 5.

Additional mapping techniques using EELS fine structure and MLLS

For further examples of the MLLS approach to signal extraction and mapping, please refer to the article on advanced spectral mapping techniques in issue 14 of our KnowHow publication, accessible via the following link:

http://www.gatan.com/knowhow/knowhow14/spectral.htm

Acknowledgement

This article was originally composed by Mike Kundmann.

More Information

For further details about the GIF Tridiem line of energy filter products, please follow the links below:

http://www.gatan.com/analysis/giftridem863.php

http://www.gatan.com/analysis/gif_tridiem865.php

http://www.gatan.com/analysis/777stempack.php

References:

H. A. Brink, M.M.G. Barfels, R.P. Burgner, B.N. Edwards, *Ultramicroscopy* **96** (2003) 367.

G. Kothleitner and F. Hofer, *Micron* **34** (2003) 211.

VISIT US AT:

http://mm2009.microscopy.org

Online Registration, Hotel Reservations & Tours

REGISTER NOW!!

DON'T MISS OUT!

Registration is now open for the premier microscopy meeting of the year!

Scientists and technologists worldwide who use microscopes and microbeams will gather in Richmond, Virginia, USA this July. Join your international colleagues for symposia, tutorials, intensive workshops, short courses, roundtables and vendor sessions on emerging topics in microscopy and microanalysis.

- Nanostructured Materials
- Green Product & Biological Imaging
- Kidney Imaging
- Aberration-Corrected Electron Microscopy
- Biofilm Imaging
- Microscopy & Analysis in Forensics
- Materials Characterization—for Responsible Energy Generation & Use
- 3-Dimensional Imaging in Bio & Materials Science: Bridging Nano & Micron Scales

Located just off I-95, downtown Richmond is a day's drive from most cities on the east coast, and only 2 hours from Washington, DC.

Register NOW to save $100!

https://doi.org/10.1017/S1551929500050069 Published online by Cambridge University Press