

Atomic Elemental Mapping by Simultaneous Dual EELS and EDS

INTRODUCTION

Electron energy-loss spectroscopy (EELS) and Energy dispersive spectroscopy (EDS), coupled with scanning transmission electron microscopy (STEM) provide local chemical composition along with structure information of materials. It was widely accepted that EDS is (only) good for heavy elements detection and EELS is (only) good for light elements. With the development of EELS spectrometers and EDS detectors, EELS and EDS are able to work on both light and heavy elements nowadays though each has its own strength and detection limits. EELS and EDS could work independently, but simultaneous EELS and EDS will provide a comprehensive chemical information.

With the advancements in aberration-corrected STEM, the electron probe size is now decreased to sub-angstrom level and at the same time, the current within the probe increases enormously. Such changes make it possible to collect enough signals for analytical analysis with a tiny probe, in other words to study not only the structure by also their chemistry atom-by-atom. In this application note, we will introduce the strength of EELS and EDS first, and then demonstrate the atomic element mapping by simultaneous EELS and EDS which is available on the probe-corrected Titan located at Nanolab, Milpitas, CA. The Titan is coupled with a Cs DCOR probe corrector with up to 5-order aberration correction for sub-angstrom resolution in STEM mode. It is equipped with ChemiSTEM capability which contains a high bright and stable XFEI and four quadrant Bruker Silicon Drift Detectors for EDS

detection. It is also coupled with Gatan Enfinitum spectrometer for EELS analysis. The EELS spectrometer can be operated in single and DualEELS modes. The DualEELS mode allows two EELS spectra with different regions to be recorded nearly simultaneously. The Titan also allows simultaneously EELS and EDS collection through a high-speed STEMPack. All the features make such Titan a powerful and unique analytical TEM tool for wide applications.

ADVANTAGES OF EELS

EELS is well-known about it is sensitive to light elements detection which can be explained by its high energy resolution, large elemental cross-section and high collection efficiency. The EDS energy resolution is around 120-130 eV (for Mn K peak), while EELS energy resolution is around 1 eV with a Schottky field emission gun and could reach meV level with a monochromator. The light elements' EDS signals are low and could be absorbed by specimen itself and surrounding materials. The EDS x-ray collection efficiency is as low as a few % but the collection efficiency of EELS can be much better than 90%. Although latest EDS system could detect light elements like carbon, nitrogen and oxygen, EDS still has challenges to detect lithium and boron which play important roles in battery materials and semiconductor, respectively. On other hand, it can routinely check the presence of boron and lithium by EELS. Typical B and Li K edge EELS spectra are shown in Figure 1. With STEM-spectrum image, lithium map is also possible as shown in Figure 2 from a commercial cathode

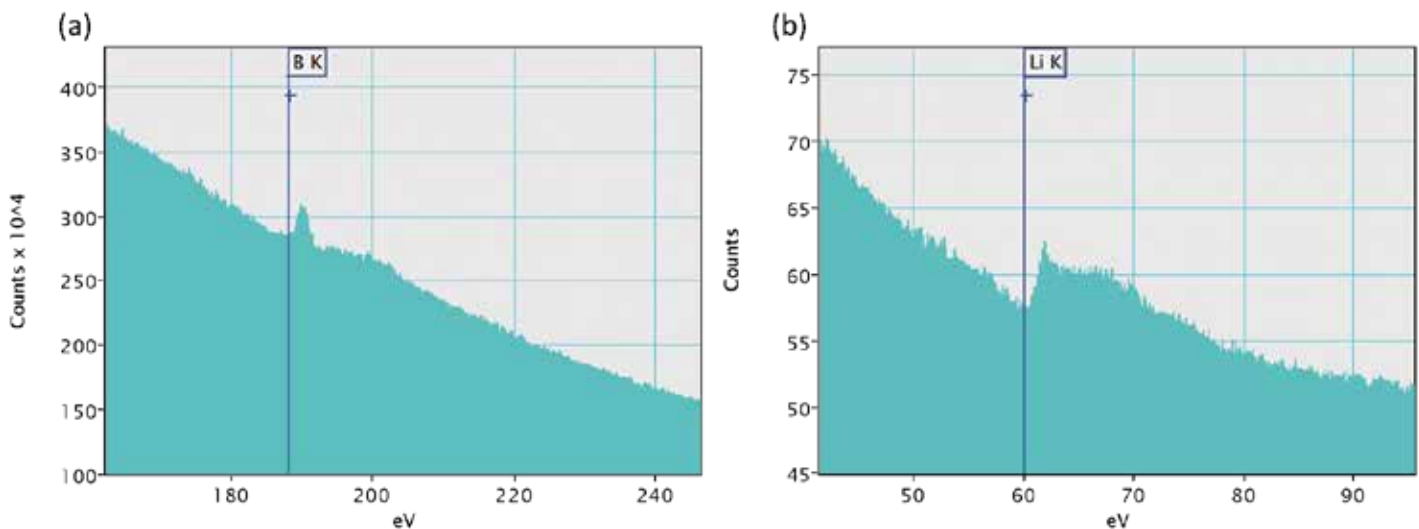


Figure 1. B-K edge and Li-K edge EELS spectra demonstrate EELS is sensitive to light elements.

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material. Lithium containing materials are usually beam sensitive and could change under electron beam. Extra attention is needed for the EELS data collection. Another Application Note will focus more about it.

Beside element identification, EELS can also provide chemical bonding information similar as XPS but with much higher spatial resolution. For example, the most common element Si in semiconductor has different EELS edge structures from pure Si and silicon dioxide (Figure 3). Such different EELS spectra can be used as their fingerprint to check their chemical states. Benefit from the aberration corrector, it is possible to study the chemical state change at nano scale. As shown in Figure 4 of a surface of LiMn₂O₄ grain, Mn L-edge shifts to the lower energy at the surface comparing to that from inside the particle. Mn L3 to L2 ratio increases at the surface. The Mn oxidation state can be determined to change from 3+/4+ inside the particle to 2+/3+ at the surface. The change of Oxygen K-edge also matches with the Mn bonding change. Such change occurs within in few nm. As the energy shift among the EELS edges of different bonds is usually small, it is very important to make sure the energy loss in each spectrum is accurate. With the DualEELS capability, the EELS can always be calibrated by the zero-loss-peak which can be included within one of the EELS regions.

ADVANTAGES OF EDS

EDS is fast, easy and sufficient to identify heavy elements and foreign elements. Though it does not have good energy resolution as EELS and can not provide chemical bonding information, EDS can get x-ray signals up to 40keV or higher. Multiple X-ray peaks can be used to identify the presence of heavy elements. EELS can only cover up to 4keV range even with DualEELS function. Also unlike EELS needs super thin samples to avoid plural scattering, EDS does not have a strict requirement for sample thickness.

EDS can have a better detection limit than EELS when considering the EDS detection efficiency has been increased dramatically with the new development of detector (such as ChemiSTEM on Titan). EELS edge is always on the tail of ZLP, the peak to background ratio will be very low especially when the target element concentration is close to the detection limit. EDS background is relatively low and consequently its Peak-to-Background ratio is much higher than that of EELS. As a result, latest generation EDS works much better than EELS for trace elements detection. One example from Titan ChemiSTEM system is shown in Figure 5. For a silicon matrix doped with low concentration P (~5at%). The EELS P-K edge is as weak as the background while the EDS P-K edge is obviously well above the background. Similar phenomena are observed on other elements like F, Cl which are widely used in semiconductor field.

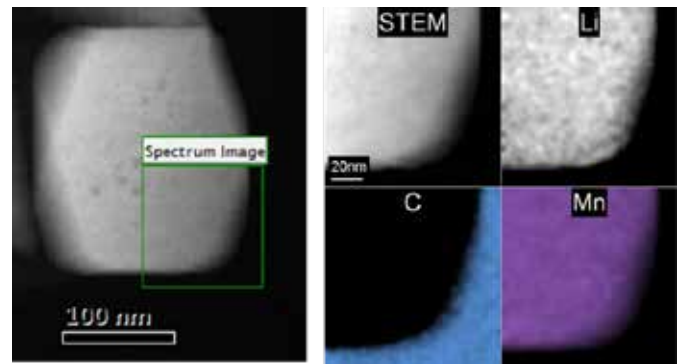


Figure 2: STEM image and EELS elemental maps of Li, C and Mn from a commercial cathode material.

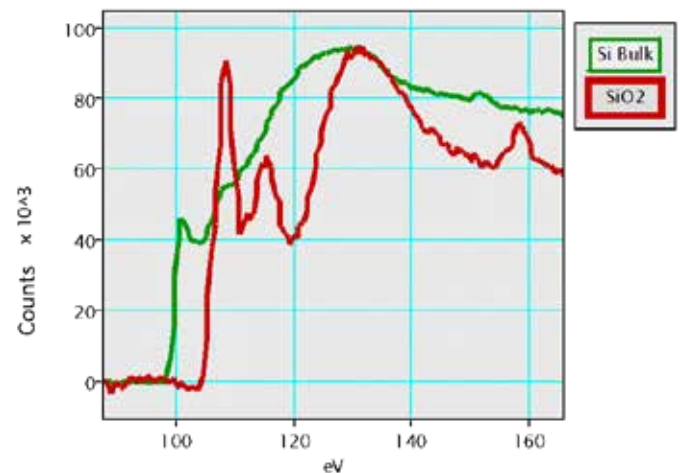


Figure 3: Si L-edge EELS spectra from pure Si and SiO₂ after background removal showing EELS can provide chemical bonding information.

ATOMIC ELEMENTAL MAPPING BY SIMULTANEOUS EELS AND EDS

Based on above two points, EELS and EDS could help each other to get a full understanding of the specimen. With the advancement of instruments and detectors, it is possible to understand the structure and chemistry atom-by-atom to enhance the fundamental properties. It was reported that atomic level elemental analysis by either EDS or EELS. But it is rare to reach atomic elemental analysis by simultaneous EELS and EDS which could provide a comprehensive chemistry information of the materials. As the Titan microscope at Nanolab is coupled with the most advanced EELS and EDS hardware and software, we here demonstrate the capability to get atomic level elemental maps by simultaneous EELS and EDS. A SrTiO₃ single crystal sample was prepared at Nanolab by conventional mechanical polishing method, which

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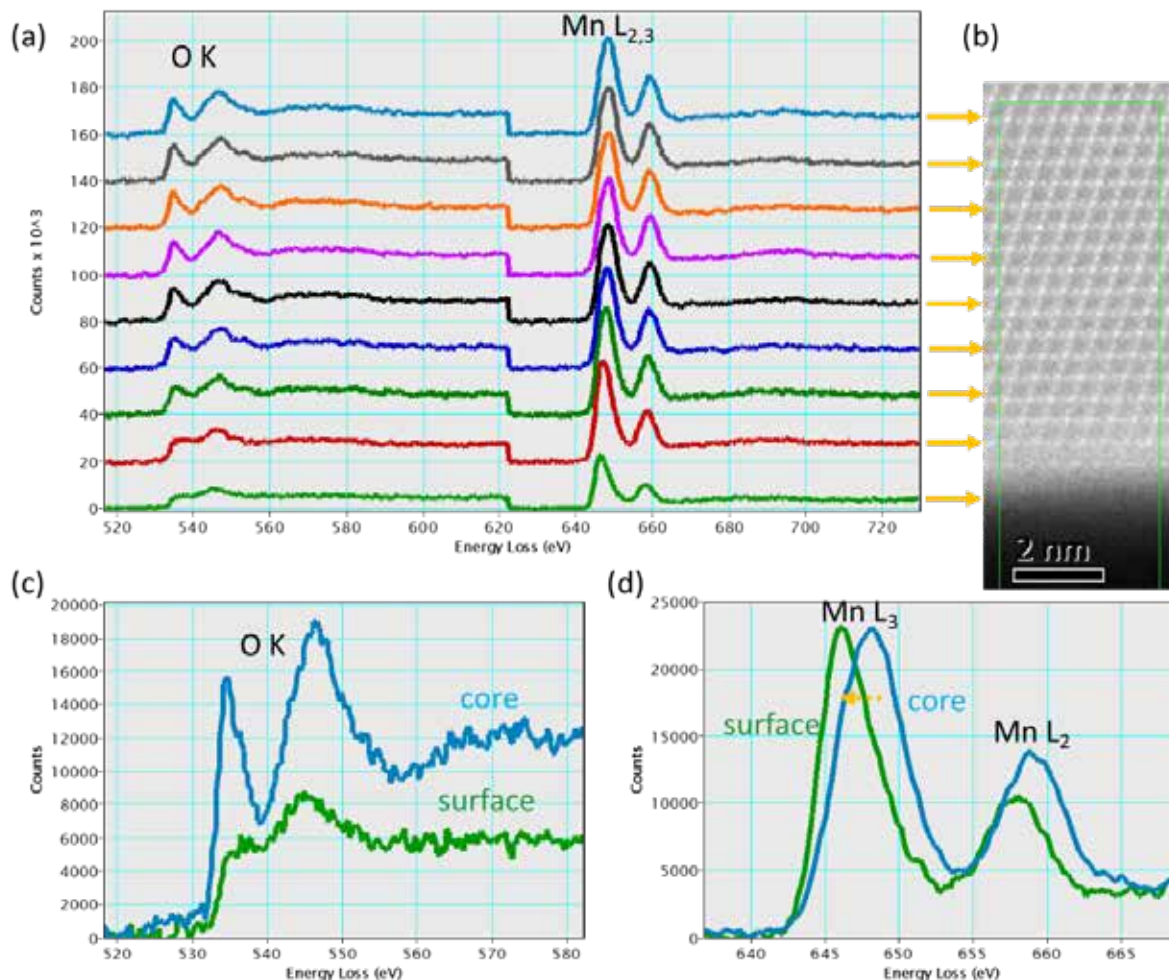


Figure 4: O-K edge and Mn L-edge EELS spectra collected from the surface and different regions (arrow) moving into the core of a LiMn₂O₄ particle. (c, d) show zoom in spectra of O-K edge and Mn L-edge from the surface and core of the particle. The changes of the O and Mn EELS spectra shows EELS is able to detect chemical bonding change at nm scale.

involves cutting, dimpling and Ar ion milling for high quality thin TEM specimen. As shown in Figure 6, both EDS and EELS results clearly show atomic elemental maps of Ti and Sr which match with their ADF image. The slight change in the contrast across the image is due to the thickness change. Both EDS and EELS give high contrast individual atom maps. The EELS maps show slightly better less noise and higher contrast compared to those by EDS qualitatively. DualEELS functions can also be combined with simultaneous EDS collection, by which there is another control of different EELS signals collection at different energy loss.

SUMMARY

Nanolab is capable of performing atomic elemental analysis by simultaneous EDS and EELS from the same region of interest. Such capability can provide the full range of chemical composition as well as chemical bonding information that cannot be obtained by any other technique at such high spatial resolution.

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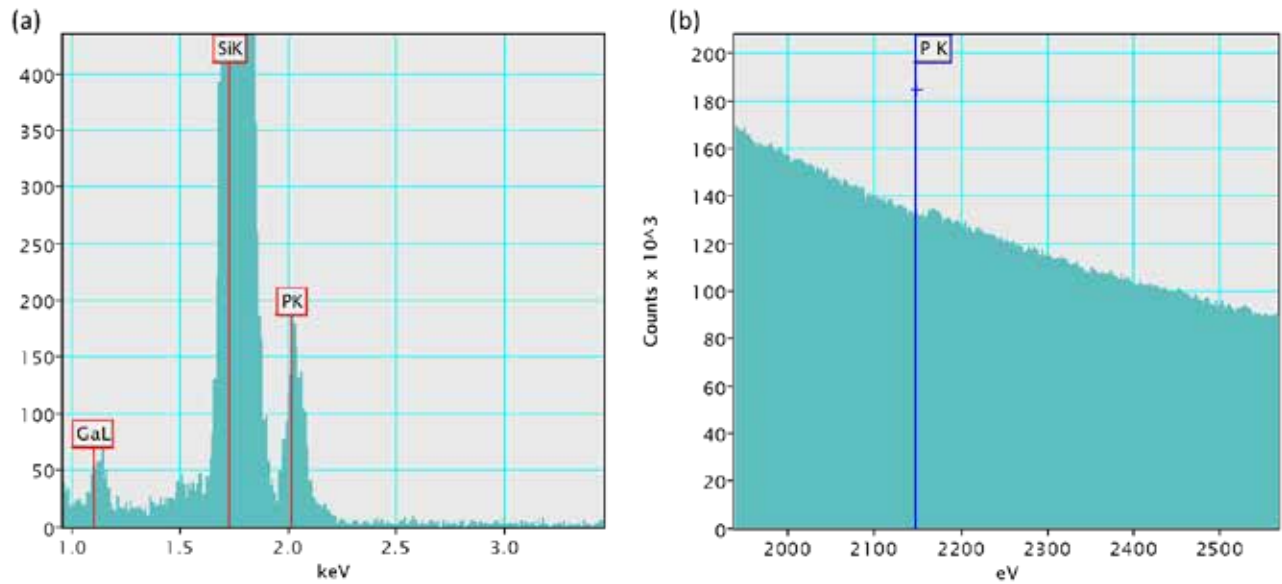


Figure 5: (a) EDS and (b) EELS spectra of P-K edge shows EDS has a higher peak to background ratio.

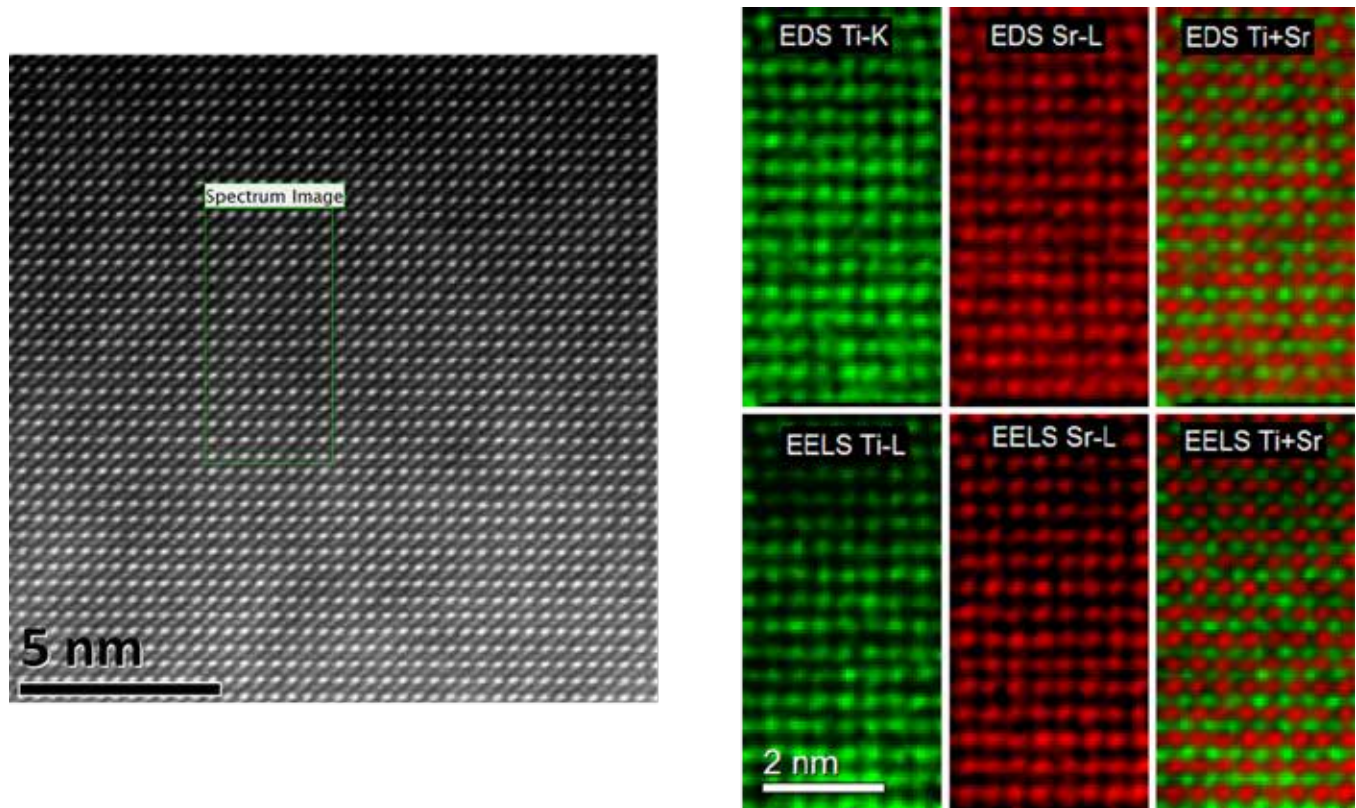


Figure 6: ADF image (left) of STO and Ti and Sr elemental maps by simultaneous EDS and EELS (right)