האגודה הישראלית למיקרוסקופיה
THE ISRAEL SOCIETY FOR MICROSCOPY

Quantitative Chemical Analysis in TEM

Ting Mao, Ruth Moshe, Hadas Sternlicht, Rachel Marder and Wayne D. Kaplan

Department of Materials Science and Engineering, Technion, Haifa, Israel

Introduction

The main analytical tools which are used for chemical composition analysis of materials in TEM are energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). While EDS reveals atomic composition only, EELS can give additional information regarding the nature of the atoms, their bonding, nearest neighbor distributions, and their dielectric response. However, for proper quantitative chemical analysis several factors have to be carefully considered, such as specimen thickness to compensate for X-ray absorption. Here extrapolation techniques are sometimes helpful. It is important to carefully determine the limit of detection for correct quantitative interpretation of the analysis data.

EDS is widely used for the detection of high-Z elements, however, for elements of low atomic number the detection is highly affected by absorption effects in the specimen and in the detector window. Thus, EELS is often used for the detection of low atomic number elements. Several techniques exist to use EDS and/or EELS for chemical analysis, such as **point analysis**, **line-scans**, or the **spatial difference technique** and its derivatives. Each method can give powerful quantitative information if properly used, as will be discussed.

Techniques

Point Analysis

- In TEM mode point analysis is done by using the condenser lens to focus the beam to a spot that is small enough to interact only with the feature desired to measure.
- In STEM mode the beam scanning is stopped and the probe is moved to the feature.
- Due to sample drift and/or probe instabilities, the ability to gather data from a desired region with a defined area is limited. In addition, a significant number of counts is required for a meaningful detection limit, and instabilities limit the number of significant counts.

- Disadvantages:
  - Time consuming;
  - Low spatial resolution due to sample drift and beam instability;
  - Analysis is often affected by sample contamination issues due to the static beam;
  - Non-expert users might interpret contamination as change in composition.
- Advantages:
  - Simple and does not require advanced expertise to preform.

Point analysis is taken from one spot **X**, as shown in the schematic illustration for example:

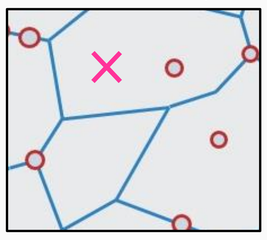

Fig.1: Schematic of microstructure showing grains and particles (occluded and at grain boundaries). The X corresponds to the spot from where EDS measurements are acquired.

Line-Scans

- Line-scans are a variation of the point analysis, in which a series of spot analyses are preformed along a line. Doing so enables to reveal the composition profile across a linear feature, such as grain boundaries, interfaces and etc. Superimposing the spectra acquired creates the spectrum line profile and allows for the measurement of compositional changes across a linear defect.
- Disadvantages:
  - Time consuming, even more than point analysis;
  - As in point analysis the spatial resolution is low due to sample drift and beam instability;
  - The line profile exhibits only one point on the interface itself. Therefore, multiple analyses are required in order to determine chemical variation along the interface.
- Advantages:
  - Simple and does not require advanced expertise to preform;
  - Since line defects are prominent features the line-scan eliminates the uncertainty of measuring contamination artifacts.
  - Good spatial resolution, but variations in sample thickness must be characterized.

Line-scan is recorded along a series of spots, as shown in the schematic illustration for example:

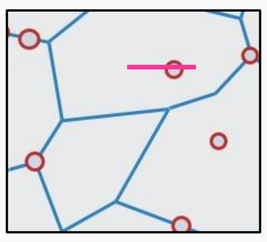

Fig.2: Schematic of microstructure showing grains and particles (occluded and at grain boundaries). The line represents a typical line scan, where matrix and particle are analyzed.

Spatial Difference

- In spatial difference analysis, spectra from a region of interest (e.g. a grain boundary), as well as spectra from the nearby matrix, are recorded [2]. During acquisition of the spectra, the beam is scanned within a rectangular area. The proportional intensity from the matrix is subtracted from that of the planar defect, and any excess intensity is then associated with excess concentration at the defect.
- Disadvantages: There is no spatial resolution to the technique, and line-scans should be acquired to resolve dopant/impurity distributions.
- Advantages: Relatively reliable option to measure small amounts of impurities at planar defects. The detection limit is certainly better than other approaches.

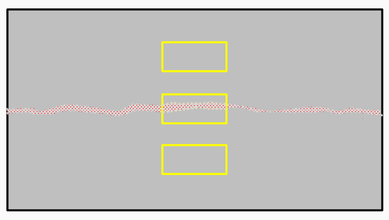

Fig.3: Schematic of a grain boundary showing rectangular boxes from where EDS or EELS measurements are performed using the spatial difference technique.

- Limit of detection [3]: $\Gamma_{\min} = \frac{V}{S}\frac{A_B}{A_A}\rho k_{AB} 3\frac{\sqrt{2I_A^b}}{I_B}$

Where V/S is the ratio of the interaction volume to the area of the grain boundary inside the interaction volume;
A_A and A_B are atomic masses for segregant (A) and matrix (B);
ρ is the density of the matrix (atoms/nm^3);
I_B is the intensity in the elemental peak for the matrix;
$I_A{}^b$ is the background intensity under the elemental peak for the segregant;
k_{AB} is the Cliff-Lorimer ratio (k-factor) based on the assumption of thin-film criterion.

Convergent Beam Spatial Difference

- The chemistry of planar defects measured using EELS or EDS in TEM mode assuming $d<<r$ and solid solubility $0<x<<1$ can be calculated using $I_s/I_m \approx x + 2d/\pi r$ where I_x and I_m are the solute and matrix intensities, x is the solid solubility, d is the effective chemical width of the planar defect with an excess of solute and r is the radius of the beam.
- By plotting the ratio of intensities between the solute and the matrix as a function of r^{-1}, a linear fit is expected, from which the effective chemical width, d, and the solid solubility, x, can be extracted [4].

- Disadvantages:
  - The radius of the beam has to be measured.
  - The interaction volume is estimated using a simple geometrical model.
  - d does not have to be uninform throughout the thickness and may depend on the local structure.
  - Limit of detection was not well defined.
  - Absorption is not taken into account.
- Advantages:
  - Requires only TEM mode.

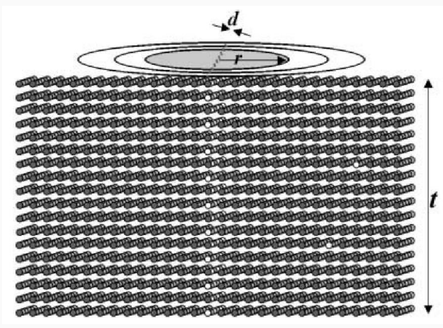

Fig.4: Schematic illustration showing the experimental parameters used for the convergent beam spatial difference method [2].

Quantitative Analysis

Cliff-Lorimer ratio approach (or the ***k*-factor**):

In a thin specimen the ratio between two constituents elements, C_A and C_B (usually defined as wt.%) is related to the X-ray intensities above the background as follows:

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

where k_{AB} is the Cliff-Lorimer factor (k-factor), which is not a constant and depends on the specific TEM/EDS apparatus and the used kV. Determination of the k-factor is the critical step for consequent quantification.

The k-factor can be determined theoretically (with large errors) or experimentally. To determine the k-factor experimentally, thin standard specimens with known composition are required. The k-factor is determined using the ratio of the measured peak intensities of the standards, whereby the peak intensity is determined by subtracting the background and integrating the peak.

For chemical analysis in TEM, the k-factor relates only to the atomic-number, and absorption effects must be quantified for thicker samples. Fluorescence effects can be neglected in thin specimens.

Limit of detection in TEM:

The general approach in TEM quantitative analysis is to define the detection limit at a 99% confidence limit of detecting a minor element, or the minimum mass fraction measurable in the volume to be analyzed. This represents the smallest concentration of an element (usually in ppm or wt.%).

The detection limit is thus a statistical principle, where a peak can be detected only if it is three times larger than the standard deviation of the background counts.

Using the k-factor, the limit of detection of an element B in a matrix A can be described by:

$$C_B^{\min} = 3C_A\frac{1}{k_{AB}}\frac{\sqrt{2I_B^b}}{I_A - I_A^b}$$

Where C_A is the concentration of the matrix A, I_A is the integrated intensity of A and $I_A{}^b$ and $I_B{}^b$ are background intensities for elements A and B.

Conclusions

- Multiple techniques are available to preform EDS or EELS quantitative chemical analysis using a S/TEM.
- For all techniques, reliable analysis requires standards of known concentration to be evaluated.
- The results can depend on the beam size, shape and stability, therefore the electron beam should be characterized during the analysis process.
- The combination of spatial difference analysis with line-scans provides data with excellent detection limits combined with good spatial resolution.

References

[1] D.B. Williams and W. Craig Carter, Transmission Electron Microscopy, chapter 4 p.615
[2] Muller D.A. Ultramicroscopy 78:163-174,1999
[3] V. J. Keast, D. B. Williams, Journal of Microscopy, Vol. 199, Pt 1, pp. 45±55, 2000
[4] T. Walther , Journal of Microscopy 215 (2004) 191-202.