In-situ Sample Preparation of Oxidizing and Contaminating Samples for High Quality EDS and WDS Quantification Using FIB-SEM

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Project Overview

Energy dispersive and wavelength dispersive X-ray spectroscopy (EDS and WDS) are very important tools in materials research to obtain information about the chemical composition of a sample. A planar and clean surface within a homogeneous material is essential to achieve a proper quantitative analysis with those methods. Often, surfaces tend to contaminate or oxidize very fast under atmospheric conditions. Usually samples cannot be transferred to the microscope without exposure to these conditions. Electron microscopes themselves provide a high vacuum free of contamination. Surfaces prepared with a focused ion beam (FIB) are smooth and sufficiently free of contamination, but are not perpendicular to the electron beam. In this work, an *in situ* preparation procedure was developed to improve the accuracy of quantitative analytical results using a FIB-SEM equipped with EDS and WDS. For this, the geometric obstacles had to be bypassed to achieve a FIB-prepared surface free of contamination or oxidization, perpendicular to the electron beam and suitable for the analysis.

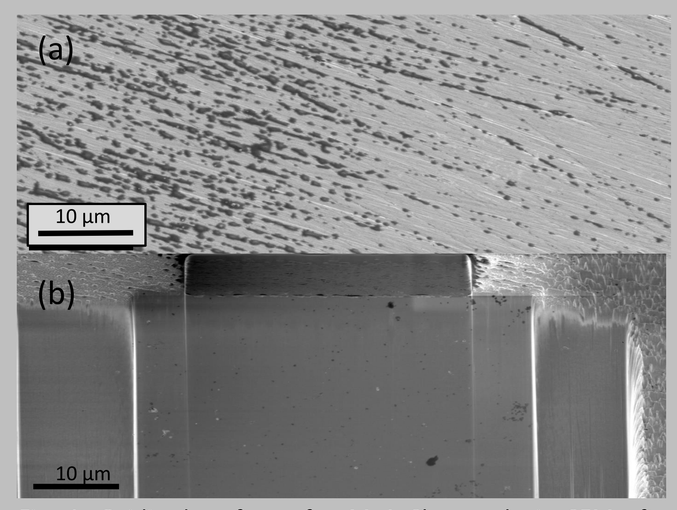

Fig. 1: Oxidized surface of a MgAgSb sample in SEM after atmospheric exposure (a) and *in-situ* FIB prepared Cross-Section (b).

WDS Quantification on an Oxidized Surface

- Measuring a sample with EDS/WDS covered by an oxidized surface layer results in wrong ZAF correction factors.
- Non normalized EDS/WDS calculations indicate possible measuring errors by deviating from a sum of 100% wt. (Tab. 1).

Oxidized Surface of MgAgSb		
Element	Weight [%]	Atom [%]
Magnesium	8.7	33.1
Silver	37.5	32.1
Antimony	46.0	34.8
Total	**92.2**	100.0

Tab. 1: EDS/WDS results of a MgAgSb thermoelectric sample with oxidized surface deviating from 100% wt. Atomic concentrations normalized.

- Omitting normalization, the quantitative values from tab. 1 results in a total elemental content of 92.2 wt.-%, indicating that elements are missing.

WDS Results with Oxygen Included		
Element	Weight [%]	Atom [%]
Magnesium	8.7	16.5
Silver	43.0	18.5
Antimony	49.3	18.7
Oxygen	16.0	46.3
Total	**117.0**	100.0

Tab. 2: Adding Oxygen to the EDS/WDS results leads also to a deviation from the sum of elemental contents of 100 % wt..

- The values in Tab. 2 show an even higher deviation from 100% wt. when oxygen is included.
- ZAF correction is not applicable for surface contaminations, thus elemental quantification with EDS/WDS is not possible.

InSitu Preparation Using FIB-SEM

- The FIB column is inclined by 52° angle to the electron column and a -38° angle from the stage surface.
- Thus, with the maximum negative stage tilt of -10° slopes of -28° relative to the sample surface are produced (Fig. 2).

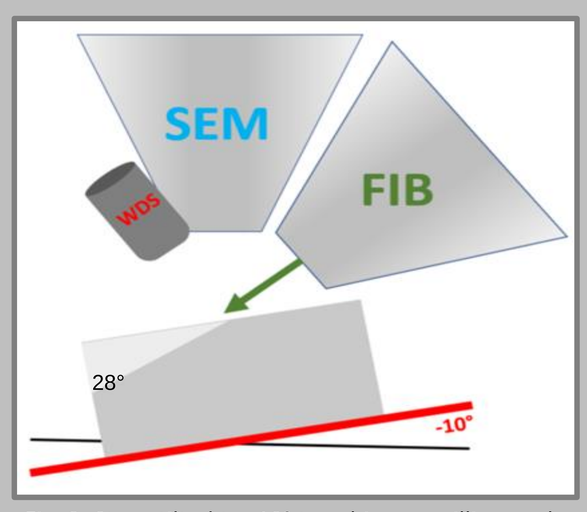

Fig. 2: Stage tilted to -10° to achieve a milling angle of -28° relative to the sample surface.

- The surface areas on which quantitative experiments are conducted needs to be perpendicular to the electron beam (90°). Therefore, the stage is tilted to +28° after the milling procedure (Fig. 3).

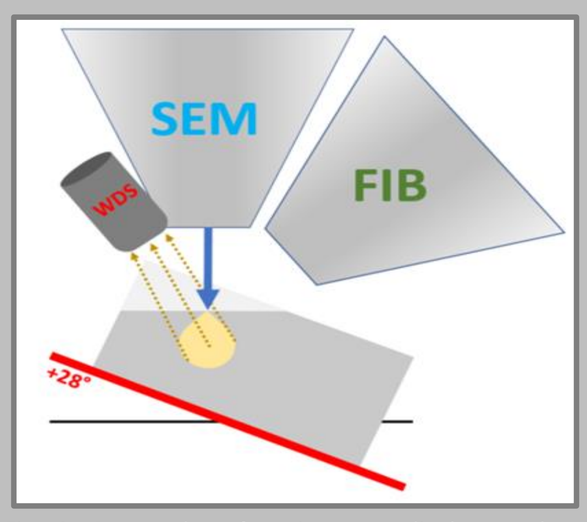

Fig. 3: Prepared surface is perpendicular to the electron beam.

- Most EDS/WDS software read the stage tilt from the microscope to correct it. It is important to make sure, that the EDS/WDS system uses the correct surface orientation for calculation.
- Region of interest, excitation volume and the surface where the X-Rays leave the sample need to be within the prepared section. Shadowing of the X-ray detectors by the section rims has to be avoided
- At our system (Impact angle of WDS 40°), this region is usually not bigger than 1-2 µm around the beam position.

WDS Quantification on FIB Prepared Section

- WDS measurement was performed on a prepared FIB-Section (Fig. 1b).
- The vacuum in the microscope (~10^{-5} - 10^{-6} mbar) prevents the sample from further oxidation.

Oxidized Surface of MgAgSb		
Element	Weight [%]	Atom [%]
Magnesium	8.8	31.3
Silver	40.7	32.7
Antimony	50.7	36.0
Total	**100.2**	100.0

Tab. 3: Quantification with EDS/WDS of a FIB- prepared surface. Wt.-% without , at.-% with normalization.

- The quantification of the FIB prepared section results in 100.2 % wt..
- The result shows a good accuracy.

Conclusion and Outlook

- This procedure enables the chemical analysis with EDS/WDS of fast contaminating samples and prevents the oxidation of sensitive specimens as no exposure to the lab atmosphere occurs.
- With this procedure, it is also possible to prepare non-planar, contorted samples like beads to prepare a flat surface perpendicular to the beam to perform EDS/WDS quantifications

Instrumentation

- FEI Helios NanoLab 600i Dual Beam
- Thermo Scientific Pathfinder with 30 mm2 UltraDry SSD detector and an MagnaRay WDS spectrometer.
- High Tension 10keV, Mg measured with WDS (TAP), Ag, Sb O measured with EDS.

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