

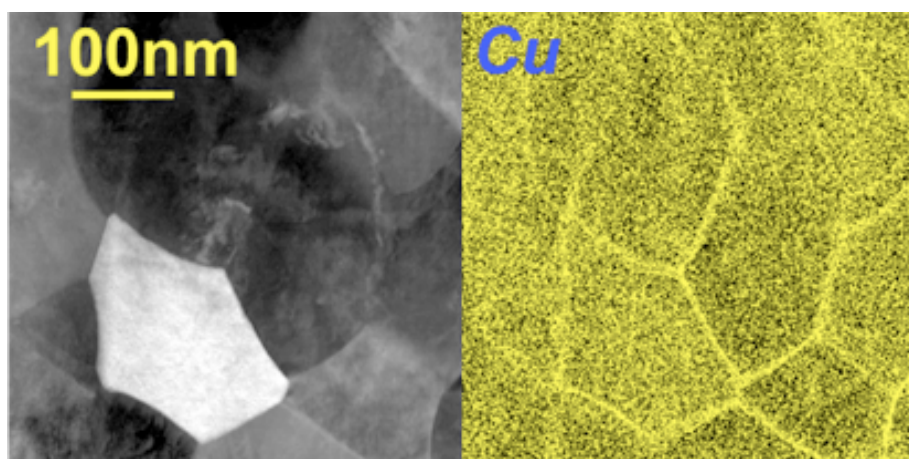
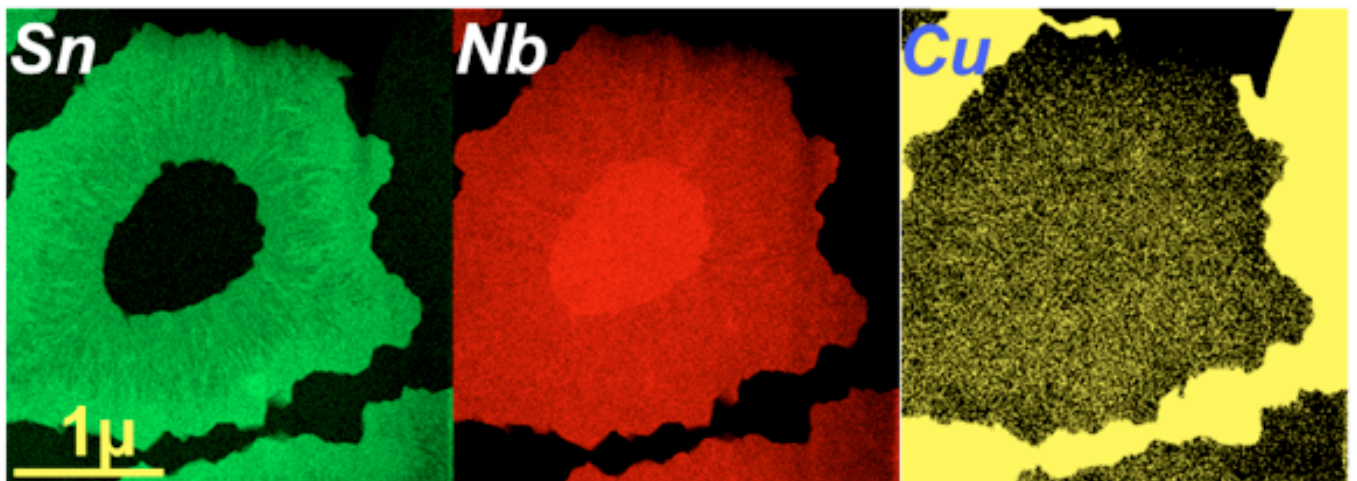


Swiss Society for Optics and Microscopy

Société Suisse pour l'Optique et la Microscopie

Schweizerische Gesellschaft für Optik und Mikroskopie

Mitteilungsblatt / Bulletin d'information 1+2 / 2013



ChemiSTEM element maps

Recent EDS instrumental advances in STEM: from principles to applications

Introduction

The electron microscopy community makes a wide use of Energy Dispersive X-ray Spectrometry (EDS) for elemental mapping in STEM. This technique was however long reckoned slow, dozens of minutes if not an hour, to collect enough information for one map.

Recent instrumental advances have dramatically changed the situation, reducing the acquisition time to minutes, improving the maps quality and boosting their spatial resolution beyond the nanometer scale or even down to the single atom column in crystalline materials. This opens the way to true composition mapping – no longer raw counts mapping –, interface quantitative analysis and soon EDS tomography to extract chemical composition of buried nano-objects.

The major progress

Step 1: Improving the X-Ray production with better electron source

A higher electron probe current or a thicker sample is required to produce more X-rays. However, increasing thickness rapidly degrades the spatial resolution due to beam spreading through the sample. Even the effort is rather opposite to produce thinner samples (a very few tens of nm) for imaging atom columns or interfaces seen edge-on. The first key point to get intense electron probes is a high gun brightness β – not the total emitted electron current – that links the current i emitted by a source of diameter d within a solid angle corresponding to a cone of semi-angle α :
$$\beta = 4i/\pi^2 d^2 \alpha^2$$

From optics laws, this quantity is constant throughout the whole path of electrons as long as no absorbing media is met (lenses, apertures do not change it!). So the same equation holds when i , d and α are considered at any level between the gun and the impact point on the sample. If the operator wishes to increase the probe current i and decrease its diameter d , it leads to an increase the convergence angle α ... that rapidly blurs the probe due to spherical aberration.

Since the eighties, analytical TEM/STEMs use mainly "field emission" Schottky guns (however not really *field emission*!) which bring $\sim 4 \cdot 10^8$ A/cm²sr at 200kV. FEI made a step forward four years ago by redesigning its Schottky gun and boosting the brightness of the X-FEG that fits the Osiris and Titan microscopes line ($2 \cdot 10^9$ A/cm²sr at 300 kV). At the same time, JEOL chose to develop a more stable cold field emission gun for its ARM200F analytical microscope.

One should note that while gun brightness, spatial resolution and possibly irradiation damage increases with accelerating voltage, the ionization cross-section decreases. Thus, one should seek the optimum accelerating voltage for each material and sample thickness.

Step 2: Improving the X-Ray production with better probe forming optics

A spherical aberration corrector for illumination is also present on the Titan, ARM200 and H-2700. It helps keeping thin probes while the probe current, and thus the convergence angle α , is increased. Nowadays HRSTEM resolution is better than 0.1nm at some tens of pA probe current and 0.2nm at 2nA (0.1MW/cm²!). The chromatic aberration and often the sample irradiation damage are now the limiting factors to get still higher beam current in thin probes.

Step 3: improving the X-ray collection

The maximum counting rate of EDS systems has increased during the last decade by a factor of at least 20 times by replacing the Si(Li) detectors (Silicon Lithium drifted) by SDD detectors (Silicon Drift Detectors). The Si(Li) uses a thick (~3.5mm) Si crystal doped under its entrance window by Li diffusion. The anode collecting the electrons resulting from the conversion of X-ray energy in electron-holes pairs has the same area as the crystal active area. That leads to a high electrical capacitance and limits the counting rate to some 3000-8000 photons/s depending on the expected energy resolution. The SDD is built on a thinner Si crystal (~0.5mm) and electrons are driven toward a small anode by a set of electrodes resulting in a much smaller capacitance that boost the maximum counting rate to at least 50'000 or even more than 100'000 counts/s. However the highest count rates are never attained – even with the brightest electron guns – with probes used to tackle the nm and very thin samples used for atom column EDS mapping. Moreover, the SDD detector becomes partly transparent to X-rays above 10 keV and its detection efficiency drops by 50% at 20 keV compared to the Si(Li) for instance.

The main weakness of the EDS system remains the poor collection efficiency of X-ray photons. Emission of characteristic X-rays by ionized atoms is isotropic but the active head of the detector has to be small to fit the narrow space close to the objective lens pole-pieces.

EDS suppliers did efforts to increase the collection solid angle by using detectors of larger area at the expense of a slight loss of energy resolution. Efficient in the SEM, this solution has only marginal benefits in the TEM, the larger the diode the farther its position. For instance, FEI uses in Osiris and Titan the Super-Twin pole pieces (pole-piece gap 5.4mm, Cs coefficient of 1.2mm) to keep a 0.23nm HRTEM Scherzer resolution at 300kV (without image corrector) and 0.07 nm in STEM mode with a probe Cs-corrector while retaining 40° sample tilt capability. According to FEI data, the Titan can fit lateral detectors with a collecting angle of 0.13sr, though Virginia Tech claims 0.3sr/EDAX.

In 2009, FEI launched the *Super-X* concept with four built-in windowless diodes, 30mm² each, arranged around the pole-pieces and protected by shutters [1]. The total collection and take-off angles comes to 0.9sr/22° and 0.7sr/18° on Osiris and Titan respectively. The diode window removal increases that 7 or 5 times geometrical gain by another 2 times for light elements. This better efficiency improves the elemental maps quality (better statistical relevancy) at constant acquisition time or reduces the acquisition time and the irradiation dose at constant map quality.

More recently Bruker developed the *QUANTAX 400-STEM* for Libra Zeiss microscopes that gather four windowless 30mm² diodes on one side of the goniometer, two being

above the sample and the two others below. They cover together 1sr at the large 25° take-off angle. Unfortunately, this detector requires a larger EDS port than usual and cannot fit into other microscopes without special order. JEOL developed the lateral *Centurio* detector given as a 100mm² windowless (single?) diode reaching 0.98sr on the ARM200F (no details available).

The symmetrical distribution of the Super-X diodes around the microscope column axis allows quite large sample tilt (~20°...30°) without losing too much EDS signal. This situation is favorable to tomography as well as interface studies in materials where they lay normal to the thin foil plane. However looking in more detail, small sample tilt or bending may bring some diodes in (partial) shadow (fig.1). If this effect is partly offset by the better exposition of the other diodes and if it sounds negligible for element distribution maps, it may nevertheless bias quantitative analysis owing to the energy dependent absorption of X-rays at the edge of the shadowing feature (roughness or bending of the sample, edge of the sample holder).

Example 1: Improving the map quality (M. Cantoni, EPF-Lausanne)

Marco Cantoni did a comparison of Nb₃Sn superconductor maps obtained on a CM300 fitted with 10mm² Si(Li) detector (fig. 2) and ChemiSTEM (fig. 3). The material is polycrystalline and contains Cu that is expected to segregates to grain boundaries [2].

Example 2a: Improving quantitative analysis (P.A. Buffat, IC-EM AGH, Krakow)

The mechanical properties of nickel-base superalloys for high temperature and extreme environment are improved by the dispersion of nanoprecipitates γ' (type Ni₃(Al,Ti) fcc ordered) and γ'' (type Ni₃Nb tetragonal bc ordered) in the matrix γ (solid solution Ni-Cr-Fe fcc disordered). TEM dark field and HAADF/STEM give ambiguous images and only EDS maps bring the phase distribution using Al and Nb as selective elements (fig. 4). The nanoprecipitates are buried in the matrix. However several arguments (shape of profile, atom resolution EDS maps of different thicknesses samples) show that Fe and Cr are absent from the nanoprecipitates. This led to write a short routine to remove the contribution of the surrounding matrix and to extract the true γ' and γ'' composition [3].

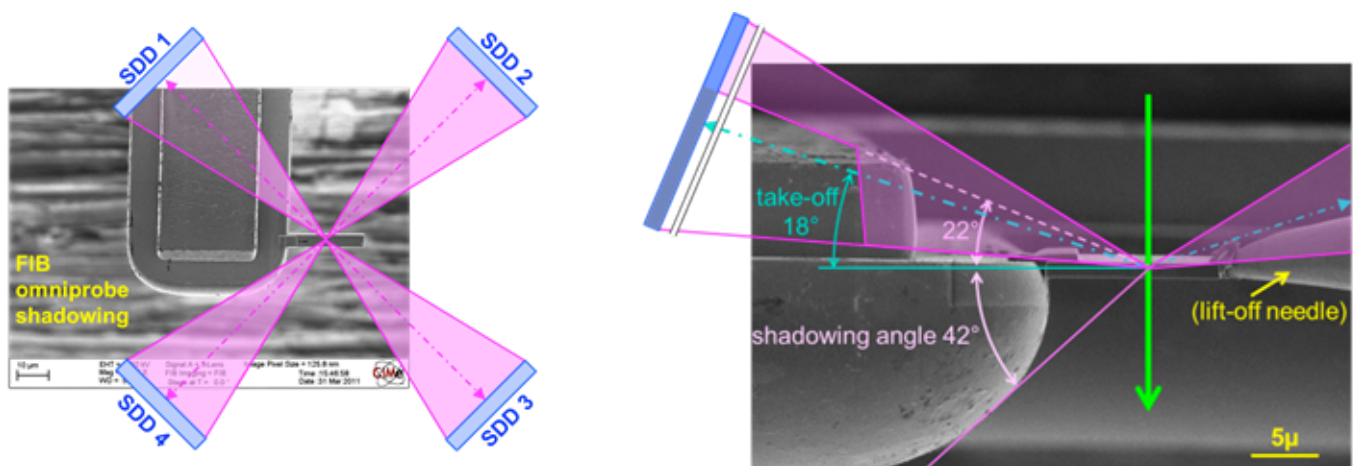


Figure 1: At least one diode is in the shade of the Omniprobe grid when the FIB lamella is mounted at the mechanically safe position. Left: view from top. Right: lateral view.

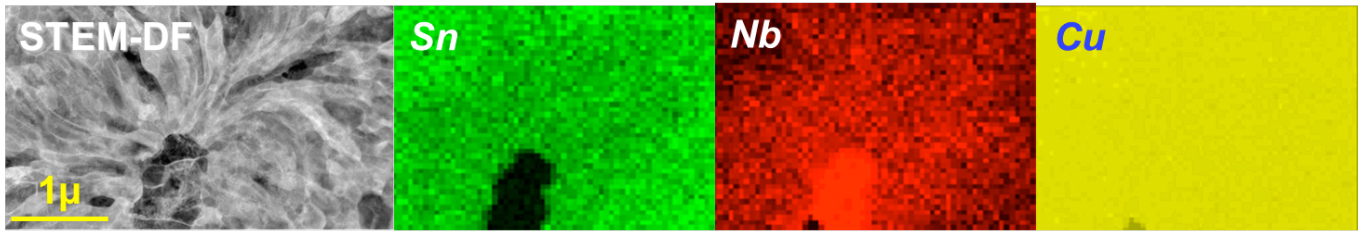


Figure 2: DF/STEM and element maps from CM300 (300kV, 1nA, 128ms dwell time, full map 128x98 pixels, 1 hour). The Cu map does not exhibit any structure.

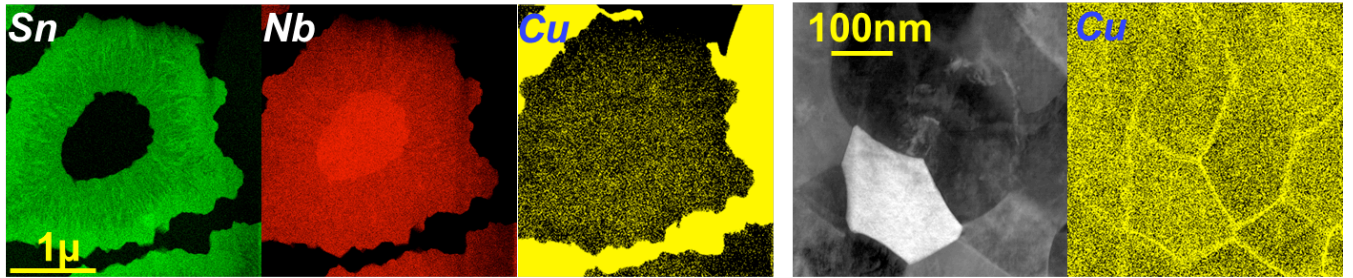


Figure 3: ChemiSTEM element maps from Osiris (200kV, 2.5nA, 4ms dwell time, 400x400 pixels, 10min). Left: Overview of a wire. Right: Cu segregation at grain boundaries.

Example 2b: Interface structure using maps at atom column resolution

EDS maps showing distinct atom columns of alloys appear significantly more delicate to obtain than for ceramics (often perovskites) or semiconductors. On the hand sample preparation is more tricky to get foils only a few tens of nanometers thick and reasonably flat. On the other hand, alloys seem more prone to electron beam damaging (fig. 5).

The original EDS map of the γ'/γ'' [010] interface (fig. 6) was averaged over the equivalent vertical rows to filter noise while retaining the composition change across that interface. The interface plane is a pure Ni plane. The γ' Al/Ti columns are facing the closest γ'' Nb columns across the interface. The first plane in γ' along the interface exhibits a dark HAADF contrast. It corresponds to a slight reinforcement of the Al atom columns contrast suggesting that Al segregation occurs. Geng has observed a similar effect using atom probe tomography [4].

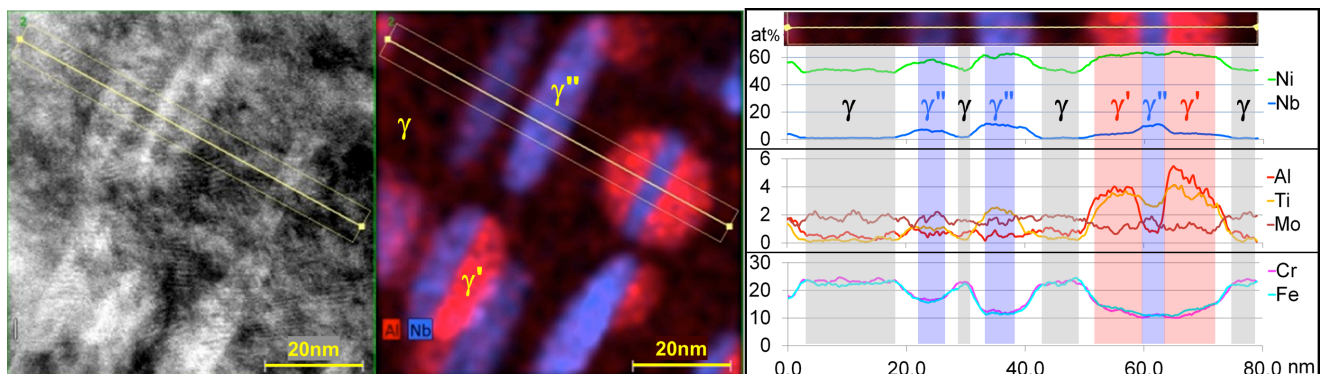


Figure 4: Left: HAADF/STEM. Centre: phase distribution Al (red) and Nb (blue) raw counts maps differentiating the 3 phases. For the particular heat treatment used here, γ' and γ'' join on a $(001)_{\gamma''}$ plane to form so called "*compact morphology particles*". Right: the linescan shows that unexpectedly Nb and Ti are present in γ' and γ'' respectively. (200kV, 430pA, 10mrad, 17min)

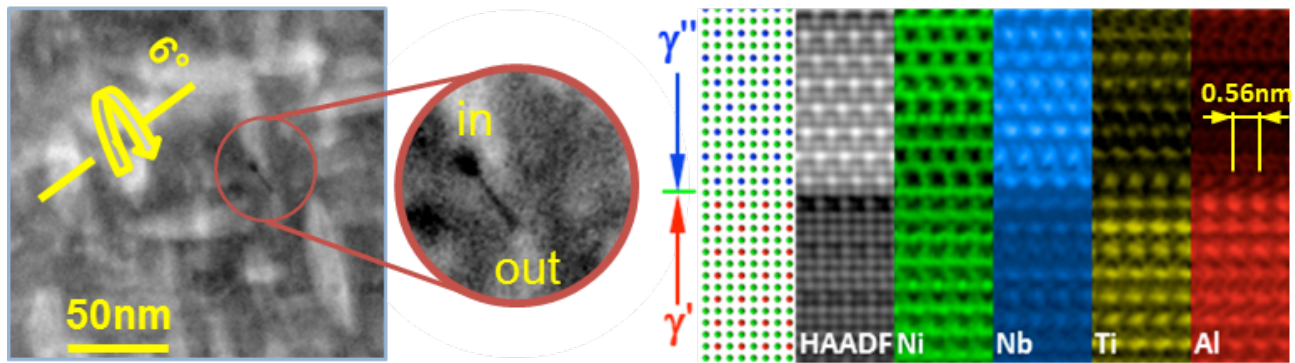


Figure 5: Hole drilled by a 0.1nm probe standing ~2s (300kV, 120pA, 25mrad,).

Figure 6: Model, HAADF and element maps of a γ'/γ'' interface (200kV, 220pA, 16mrad, 330s).

Conclusion

The main limits of EDS using ChemiSTEM or equivalent system is nowadays the resistance of the sample to electron irradiation and the need for better quantification software, in particular for standardless analysis (better Cliff-Lorimer factors or moving to the zeta method [5]).

Nowadays, the EDS mapping competes or even supersedes the EFTEM and ELSI mapping for elemental analysis with exception of the ultra-light elements (Li, Be, B). Moreover it does not come up against unfavourable or delayed edges (Al in the example above for instance) and is significantly more accessible to a wide range of users.

References

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