Towards single atom sensitivity in the analytical TEM

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In many scientific areas and application fields the reliable detection of small amounts of material is paramount. For instance, the analyses of dopant profiles in semiconducting devices or of metal diffusion into organic semiconducting layers require not only suitable microscopes, but also analytical equipment with high detection efficiency. Conventional (integral) analytical methods relate trace elements with concentrations in the ppm or ppb range or below. However, these concentrations are still very large numbers in terms of the number of atoms (1 ppb corresponds to roughly 10^{12} atoms). In a transmission electron microscope (TEM) the number of analyzed atoms is typically quite small when working at high spatial resolution. On the other hand, the analytical sensitivity using electron energy-loss spectrometry (EELS) or energy-dispersive X-ray spectrometry (EDXS) will typically only reach the range of 0.1 at%. When taking into account the overall number of analyzed atoms (e.g. analyzed area on specimen 1 nm^2, specimen thickness 50 nm), 0.1 at% will correspond to just a few atoms (e.g. 3).

While atomically resolved elemental maps acquired by EELS have been around in the literature since a couple of years, EDXS could not yield this kind of information until recently (for an overview about the current status in the field of spectroscopic imaging at high spatial resolution see [1]). This is mainly because EELS does not suffer from narrow detection solid angles and small fluorescence yields, which limit the number of detected X-rays.

It was the combination of a bright electron source, a spherical aberration corrector for the probe, and an X-ray detector with a large solid angle that made it possible to obtain atomically resolved 2D information about elemental distributions (FEI's ChemiSTEM technology) [2]. In particular, new X-ray detector designs with large area silicon drift detectors (SDD) improved the detection efficiency by an extent that the sensitivity of EDXS is approaching single atoms. The high solid angle (0.7 sr) in combination with a small spot size and high beam current (due to spherical aberration correction) will increase the detection efficiency easily by a factor in the order of 20 or more compared to standard systems. This increase significantly improves detection sensitivity and the minimum detectable mass fraction (MMF) making single atom detection feasible.

At our institute the ASTEM (Austrian scanning transmission electron microscope) was installed recently. Around the core instrument, a probe corrected Titan^3 G2 60-300 from FEI, it features a high brightness Schottky type electron emitter (X-FEG, FEI), a high solid angle windowless SDD X-ray detector (Super-X, FEI [3, 4]), and a Quantum type imaging filter (Gatan [5]). This system not only offers very high spatial resolution in STEM (< 70 pm), but also very good detection efficiency for both EDXS and EELS signals. In particular the fast simultaneous acquisition of EDXS, dual range EELS, and HAADF signals, makes it a powerful analytical instrument able to detect very small quantities of elemental species.

In this work we present simulations as well as experimental results demonstrating the ability to not only visualize but also analytically detect a small number of atoms in a sample. In figure 1 we show our first result of an atomically resolved EDXS elemental map obtained from a GaN sample [6]. Figure 2 shows an EDX spectrum of a NIST glass standard (NIST 611). This sample contains small amounts (around 500 ppm) of 61 elements and is perfectly suited to estimate minimum detectable mass fractions. For instance, from the spectrum in figure 2 (acquisition time 300 s) a 70/100 ppm MMF was estimated for Mn/Cr (in both cases using the K-lines). Recalculating these values for a situation with the finely focused high-current beam available in the ASTEM the determined MMF will reach values close to a single Mn or Cr atom. This sensitivity corresponds

nicely with EDX spectrum simulations. In addition, results from a highly doped silicon wafer (Sb concentration 2x10^{15}/cm^2) will also be shown as well as investigations of some other application related samples [7].

References

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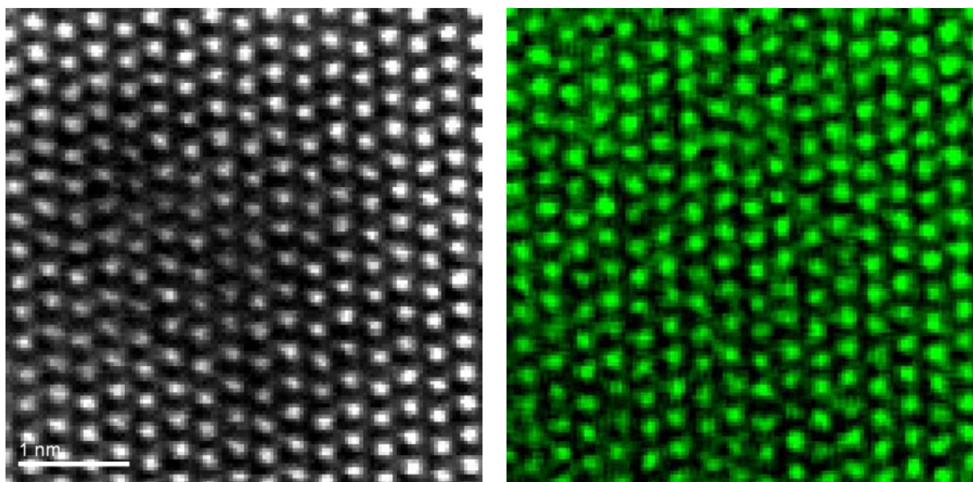

Figure 1. *Atomically resolved Ga EDXS map of a GaN sample (110 zone axis): left HAADF image, right: Ga elemental map extracted from an EDX spectrum image using the Ga-K X-ray line (data slightly smoothed). Unfortunately, during the exposure the sample suffered from beam damage.*

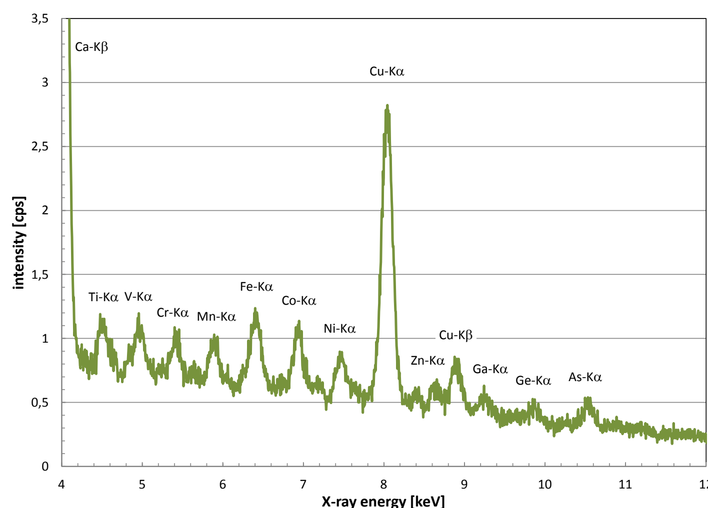

Figure 2. *EDX spectrum of NIST standard sample 611; acquisition time 300 s. The small X-ray peaks correspond to elemental concentrations of about 500 ppm.*