Comparison of experimental and theoretical X-ray intensities from (In)GaAs specimens investigated by energy-dispersive X-ray spectroscopy in a transmission electron microscope

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Abstract. Experimental measurements of X-ray line intensity ratios in a transmission electron microscope are compared over several orders of magnitude of sample thicknesses, from the nm- to the mm-range, with Monte-Carlo simulations using two different software packages. It is shown that the form of the thickness dependence of the K/L ratio of characteristic X-ray lines for GaAs is reproduced qualitatively, but the numerical differences between software packages are large. A scheme is presented for improving the simple k-factor method, taking explicitly into account the thickness dependence that remains even after application of the usual absorption and fluorescence corrections. This is done in first-order approximation by linear regression. The improvement in determining the correct indium concentration in specimens of InGaAs is calculated to be 1at%.

1. Introduction
Microanalysis by energy-dispersive X-ray spectroscopy (EDXS) in a transmission electron microscope (TEM) offers much higher spatial resolution has than in a scanning electron microscope (SEM) but suffers from poorer counting statistics. The simplest approach for quantification is the use of k-factors, i.e. experimentally determined sensitivity factors [1]. More accurate quantification of elemental concentrations depends on the knowledge of the relative ionisation cross-sections of the corresponding elements (Z-effect), modelled already in 1930 by Bethe [2] and later refined by Duncumb and Reed [3], and proper corrections for absorption (A) [4] and for fluorescence (F) [5], which can be combined for a given specimen thickness and density in the so-called ZAF-correction. For SEM studies of bulk samples at moderate voltages full self-consistent spectrum modelling has become available which allows the user to model X-ray generation as a function of the product of mass and thickness and then integrate the result over the specimen thickness, e.g. with the PROZA96 [6] program. For TEM, however, these approaches have not been implemented so far, as sample thicknesses are often not well known, while in SEM they can simply be set to \( \infty \) for bulk. This study shows how the conventional ZAF approach for EDXS in a TEM can be improved for a given material system using re-calibration based on linear least-squares fitting data recorded over a wide range of sample thicknesses.

2. Comparison of Monte Carlo Simulations to Experiments
Monte Carlo simulations of electron scattering and X-ray generation as a function of foil thickness have been carried out using two different software codes. The freely available software code CASINO
(version 2.4.2) [7], with default settings as described in the user manual, using tabulated values of the Mott scattering cross-section [8] and new calculations of the stopping power at low energies with a cut-off at 50eV [9] is a fast program to calculate L- and K-line intensities in non-relativistic approximation and is widely used for EDXS in a scanning electron microscope at voltages up to 30kV. The commercial HURRICANE code uses relativistic cross-sections as in [10], allows more complex geometries to be simulated and M-, L- and K-line intensities to be modelled, but it is much slower.

In order to study the effect of the depth at which a certain feature of interest is located within a medium-thick specimen (top-bottom effect) a model specimen for simulations was created that consisted of 2nm thin layers of a given element embedded in 200nm GaAs at a certain depth, \( d \), with 1nm of carbon coating at each surface. The acceleration voltage of the electron beam was set to \( U = 200 \text{kV} \). The X-ray detector was assumed to form a take-off angle with the specimen of \( \theta = 90^\circ \) (vertical take-off). Figures 1 and 2 show the decrease of the analytical signals for various X-ray lines, due to the increasing absorption effect as a function of depth in the GaAs specimen. While the curves obtained from the CASINO simulations can be fitted by simple exponentials [11], the corresponding curves calculated with the HURRICANE software are much noisier and reveal different trends, as can be seen from Figure 2. While soft X-rays such as N\(_K\) also decay exponentially, harder X-rays such as the Al\(_K\) do not attenuate appreciably or even increase in intensity with embedded depth. The latter trend is seen for the In\(_L\) line and probably due to the increased stopping power of electrons that have sufficiently slowed down when they approach the bottom half of the GaAs crystal.

If it is to be decided which software models electron scattering and X-ray production at 200kV more realistically, a comparison with experimental data has to be performed. Figure 3 compares the As\(_K\)/As\(_L\) ratio of GaAs modelled using both software codes, to experimental measurements using a JEOL 2010F field-emission TEM operated at \( U = 197 \text{kV} \) equipped with a Si:Li detector with ultrathin window and Oxford Instruments LINK ISIS300 software (rev. 3.2). The take-off angle was \( \theta = 20^\circ \). An aperture to suppress hard stray X-rays was used. The GaAs specimen was a wedge cleaved on \{110\} planes and mounted on a copper grid such that it could be imaged near (-4° off) a [001] zone axis so that, due to the geometry of the specimen, the sample thickness was always given as twice the distance from the specimen edge observed in scanning TEM mode. No ‘hole count’ correction was applied as the in-hole signal was very weak anyway. Secondary fluorescence by the copper support was taken into account by explicitly including the Cu lines into the quantification. Both software packages
predict qualitatively similar curves, with a transition from a plateau at small thicknesses (hardly any absorption of both lines) towards another plateau at much higher values (where both lines are equally absorbed), which occurs at a specimen thickness of \( \sim 1\mu m \) where the absorption of the softer L-line becomes relevant. However, the ratio produced by the (non-relativistic) CASINO code is \( \sim 30 \) times higher than that by the HURRICANE code. Even if the difference in detector efficiency for both lines has not been taken into account here, this can be estimated from [12] to only account for a factor of \( \sim 0.8 \), so that the CASINO simulation looks more realistic than the HURRICANE simulation.

![Graph showing AsK/AsL ratio vs. GaAs thickness](image)

**Figure 3.** Comparison of AsK/AsL X-ray ratio in GaAs vs. thickness from experiments (red triangles) with simulations using CASINO (green diamonds) or HURRICANE code (blue squares).

![Graph showing GaK/AsK ratio vs. GaAs cleaved wedge thickness](image)

**Figure 4.** Experimental result of measuring the GaK/AsK ratio for cleaved GaAs using the LINK ISIS300 software, assuming a thickness of \( t=100\)nm throughout (red squares) or the true thickness (blue triangles).

![Graph showing InL/AsK ratio vs. InAs cleaved wedge thickness](image)

**Figure 5.** Experimental result of measuring the InL/AsK ratio for cleaved InAs using the LINK ISIS300 software, assuming either a thickness of \( t=100\)nm throughout (red squares) or the true thickness (blue triangles).

Figures 4 and 5 show experimental concentration ratios of Ga/As for GaAs using both K-lines (Fig. 4) and In/As for InAs using the In L- and the As K-line (Fig. 5). The ratios were again determined for
cleaved wedges. For the square data points in red a universal thickness of $T=100\text{nm}$ was used for quantification using the LINK ISIS300 software, as could be used for cases where the true thickness is finite but not precisely known, while for the triangular data points in blue the true thickness was used for each measurement. Had the $k$-factors of the elements been correct, then the extrapolated curves should have intersected the vertical axes for zero thickness ($t=0$) at unity to reproduce the stoichiometry of the compounds. The fact the values extrapolated for $t=0$ are both too large ($\text{Ga}K/\text{As}K=1.19$ for GaAs and $\text{In}L/\text{As}K=1.12$ for InAs) confirms the corresponding $k$-factors for thin film approximation are incorrect by more than 10%. Also, had the correction for absorption and fluorescence worked properly, then the curves for the true crystal thicknesses should have produced identical and constant values, independent of thickness. The curves measured taken the thickness effects into account, however, clearly have remaining slopes and thus demonstrate that the absorption and fluorescence corrections by the LINK ISIS software are insufficient. For GaAs it reduces the slope marginally, while for InAs it overcompensates the negative slope, yielding a curve of positive slope.

### Table 1. Result of linear regression fitting to the data shown in Figures 4 and 5

| material | GaAs | InAs |
|----------|------|------|
| thickness used for fit | $T=100\text{nm}$ | $T=t$ | $T=100\text{nm}$ | $T=t$ |
| lin. correlation coefficient, $R$ | +0.9798 | +0.9697 | −0.7989 | +0.7136 |
| vertical axis intercept | 1.182±0.027 | 1.202±0.025 | 1.125±0.021 | 1.106±0.022 |
| slope of fit [$10^{-5}/\text{nm}$] | 245±14 | 162±14 | −113±22 | 89±23 |

As a consequence, if the specimen thickness is roughly known, say to within ±100nm, the curves of Figures 4 and 5 allow the user to obtain the correct Ga/As and In/As ratios to 2% relative error, as given by the uncertainties in the intercepts and a small contribution by the slopes in Figures 4 and 5. For a ternary compound of $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ of unknown chemical composition $x$ but known thickness $t$ the indium concentration in the group-III sub-lattice can be determined to better than ±1at% ($\Delta x=±0.01$).

### 3. Summary

It has been shown that absorption/fluorescence corrections applying commercial software to experimental energy-dispersive X-ray microanalysis spectra can have relative errors larger than 10%. This can be improved by making systematic measurements of relative X-ray intensities as a function of known sample thickness and fitting the remaining thickness dependence to first order. For the $\text{In}_{x}\text{Ga}_{1-x}\text{As}$ system this means the indium concentration thus calculated is accurate to better than 1at%.

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