An improved approach to quantitative X-ray microanalysis in (S)TEM: thickness dependent $k$-factors

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Abstract.
Quantifying energy-dispersive X-ray (EDX) spectra acquired in a transmission electron microscope can produce inconsistent and unreliable results even if correct values for specimen thickness and density are being used for calculating an appropriate absorption and fluorescence correction. This can be due to various factors, such as incorrect $k$-factors, faulty absorption corrections due to specimen roughness, specimen buckling or wrong estimates of the detector’s take-off angle, complicated fluorescence effects not accounted for in the software etc. For a thorough investigation of the InGaAs system, wedge shaped specimens were cleaved from GaAs and InAs wafers and studied by EDX spectroscopy in a JEOL2010F instrument, with thicknesses ranging from a few nanometres up to several microns. The thickness dependence of the relative intensities of X-ray lines that remains after nominal absorption and fluorescence correction were taken into account could be used to perform linear least-squares fits, thereby eliminating to a first order the apparent remaining thickness dependence of the $k$-factors. The resulting fits demonstrate this correction improves the quantification of the chemical concentrations of indium and gallium in InGaAs samples of known thickness to 1at%.

1. Introduction
X-ray microanalysis of bulk materials in scanning electron microscopy (SEM) can be quantified by taking into account the different fluorescence yields of the elements, the absorption and fluorescence effects of the various X-ray lines produced, the transmission of the detector window and the detector geometry. As the target is bulk-like, the complete interaction volume between electrons and X-rays needs to be taken into account, either by modelling or by parameter fitting [1]. 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. More recently, 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.

X-ray microanalysis of thin specimens in transmission electron microscopy (TEM), on the other hand, has the advantages of higher spatial resolution and the possibility of using a thin film approximation in the form of so-called $k$-factors that are simply experimentally determined sensitivity factors which are the product of the relative fluorescence yields of the various elements and the
detector sensitivity [7, 8]. For thin layer structures at different depths within a thicker specimen, the top-bottom effect should be taken into account as well, although this problem may be solved by recording two spectra at different take-off angles [9]. For medium-thick specimens in the range 10nm<\(t<1000\)nm or low take-off angles, absorption and fluorescence must be taken into account and should in principle yield consistent results for homogeneous material analysed at different thicknesses (although, not necessarily the right result!).

Testing this on our JEOL 2010F electron microscope operated at 197kV with Oxford Instruments Si:Li detector and ISIS 300 software the consistency of the thickness correction is not perfect, as the results obtained for a homogeneous specimen do slightly depend on the specimen thickness being used despite absorption and fluorescence having been taken into account. For a more thorough investigation, wedge shaped specimens were cleaved from GaAs and InAs wafer material and studied by energy-dispersive X-ray spectroscopy. In order to fit into the 2mm gap in the URP pole piece of our JEOL 2010F, the specimens were glued at 45\(^\circ\) orientation with silver epoxy dag onto copper grids specially cut out so that the wedges stuck out symmetrically on both sides. The \{110\} cleavage facets formed 90\(^\circ\) wedge specimens that could be investigated near \(<100>\) zone axes orientations. In this geometry the local thickness is given by twice the distance from the specimen edge [10]. The thickness ranges investigated covered several nm up to several \(\mu\)m. The remaining thickness dependence of the relative intensities of X-ray lines could be used to perform linear least-squares fitting, thereby eliminating to a first order the apparent remaining thickness dependence of the \(k\)-factors.

2. Experimental

Figures 1 and 2 plot the apparent concentration ratios of elements in GaAs (Fig. 1, left) and InAs (Fig. 2, right) specimens, based on peak integration of various X-ray lines using the corresponding \(k\)-factors of the ISIS 300 software and assuming either a constant thickness of \(T=100\)nm (a typical thickness of TEM specimens; red squares) or modelling the local thickness correctly as twice the distance from the specimen edge (blue triangles). As peak fitting and built-in \(k\)-factors were unavailable in the software above 20kV energy, for the In \(K\)-lines at 24-27kV the literature value of \(k_{InK}\)=7.99 was used which, however, had a massive error bar of \(\pm1.8\) (i.e. 23\% relative error) attached to it [13]. Also, intensity ratios were calculated in this instance from the peak heights rather than by peak integration and background subtraction, using a program outside the ISIS software. This curve is shown by green circles at the top of Figure 2.

Had the \(k\)-factors of the elements been correct, then all extrapolated curves should have intersected the vertical axes for zero thickness at unity to reproduce the correct stoichiometry of the compounds. Had the corrections for absorption and fluorescence worked properly, then all blue curves for the true crystal thicknesses should have produced constant values of zero slope, independent of the actual thickness. Obviously, both \(k\)-factors and absorption/fluorescence corrections are not very reliable.

Results from linear fitting the curves in Figures 1 and 2 are reported in Tables 1 and 2. It can be seen that for GaAs the remaining thickness dependence is linear to good approximation for all three blue curves, while for InAs there seem to be non-linearities at small thicknesses, which could be artefacts due to improper cleavage and hence wrongly estimated thicknesses near the crystal edges. While for GaAs the \(k\)-factors were wrong by 19\% relative for Ga\(_K\)/As\(_K\), and much more for Ga\(_L\)/As\(_L\) and Ga\(_L\)/As\(_L\), the \(k\)-factors for InAs were not out by so far. However, only after least-squares fitting could the relative uncertainties for all \(k\)-factors be brought down to 3\% and that of the slopes down to \((1.7\pm1.5)\times10^{-3}\)nm\(^{-1}\). For GaAs, it is advisable to use Ga\(_K\)/As\(_K\) and/or Ga\(_L\)/As\(_L\) the \(k\)-factors of which can be corrected to 2\% accuracy, and the remaining slopes are small enough to change this by only \(~1\%) if the thickness is known to 100nm accuracy. For InAs, on the other hand, it is best to use the mixed In\(_L\)/As\(_K\) ratio, with a similar result. The typical and maximum relative errors would be \(~2\%) and \(~3\%) respectively, for the Ga/As and In/As ratios; hence, for ternary In\(_x\)Ga\(_{1-x}\)As it should be possible to determine the In concentration \(x\) in the group-III sub-lattice to better than \(\pm1\)at\% (\(\Delta x=\pm0.01\)) using
cross-checks based on the above methods (i.e. determining the Ga/As and the In/As ratio independently and then checking the overlap region).

**Figure 1.** Experimental result of measuring the Ga\textsubscript{K}/As\textsubscript{K} ratio (above), the Ga\textsubscript{K}/As\textsubscript{L} ratio (middle) and the Ga\textsubscript{L}/As\textsubscript{L} ratio (below) for cleaved GaAs using the LINK ISIS300 software, assuming a thickness of $T=100\text{nm}$ throughout (red squares) or the true thickness (blue triangles).

**Figure 2.** Experimental result of measuring the In\textsubscript{K}/As\textsubscript{K} ratio (above), the In\textsubscript{L}/As\textsubscript{K} ratio (middle) and the In\textsubscript{L}/As\textsubscript{L} ratio (below) for cleaved InAs using the LINK ISIS300 software, assuming either a thickness of $T=100\text{nm}$ throughout (red squares) or the true thickness (blue triangles). For the In K-line no absorption was taken into account (green circles).
Table 1. Result of linear regression fitting to the GaAs data shown in Figure 1

| X-ray lines | modelled $T$ | linear corr. coefficient | vertical axis intercept | slope of fit [10^{-6}/nm] |
|-------------|-------------|--------------------------|--------------------------|---------------------------|
| Ga$_K$ / As$_K$ | $T=100$nm | +0.9798 | 1.182±0.027 | 245±14 |
|             | $T=t$     | +0.9607 | 1.202±0.025 | 162±14 |
| Ga$_L$ / As$_L$ | $T=100$nm | +0.9607 | −0.315±0.645 | 8861±329 |
|             | $T=t$     | +0.9352 | 2.117±0.100 | 426±51 |
| Ga$_L$ / As$_L$ | $T=100$nm | −0.7389 | 0.723±0.054 | −103±28 |
|             | $T=t$     | +0.7656 | 1.046±0.022 | 45±11 |

Table 2. Result of linear regression fitting to the InAs data shown in Figure 2

| X-ray lines | modelled $T$ | linear corr. coefficient | vertical axis intercept | slope of fit [10^{-6}/nm] |
|-------------|-------------|--------------------------|--------------------------|---------------------------|
| In$_K$ / As$_K$ | $T=0$     | +0.4621 | 1.071±0.036 | 44±26 |
| In$_L$ / As$_K$ | $T=100$nm | −0.7989 | 1.125±0.021 | −113±22 |
|             | $T=t$     | +0.7136 | 1.106±0.022 | 89±23 |
| In$_L$ / As$_L$ | $T=100$nm | +0.9679 | 0.957±0.024 | 372±25 |
|             | $T=t$     | −0.8271 | 0.993±0.039 | −234±41 |

3. Summary
It has been shown that absorption/fluorescence corrections applying commercial software to experimental energy-dispersive X-ray microanalysis spectra can yield relative errors above 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 In$_x$Ga$_{1-x}$As this means the indium concentration thus calculated is accurate to better than 1at%.

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