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Self-consistent absorption correction for quantitative energy-dispersive X-ray spectroscopy of InGaN layers in analytical transmission electron microscopy

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Abstract. A new method of absorption correction for energy-dispersive X-ray spectroscopy in a transmission electron microscope is tested on InGaN samples. We simulate the effective k -factor for the In L line with respect to Ga L or Ga K and plot this as a function of the Ga K/L intensity ratio, which can be directly measured from experimental spectra. This basically performs an internal self-consistency check in the quantification using differently absorbed X-ray lines, which is in principle equivalent to an absorption correction as a function of specimen thickness but has the practical advantage that neither specimen thickness nor density or mass-thickness of the specimens need actually be measured.

1. Introduction

Energy-dispersive X-ray spectroscopy (EDXS) of thin foil cross-sections in a transmission electron microscope (TEM) is an important tool to determine local elemental concentrations and often relies on simple ratio measurements [1]. Quantitative measurements in transmission geometry necessitate corrections for absorption, fluorescence and detector efficiency of the individual X-ray lines where estimates of foil thickness and density are usually required for absorption correction [2]. The thickness of the specimen can be difficult to measure experimentally, and if one knew the density precisely then the chemistry could be directly inferred. The zeta-factor method [3] can determine concentrations and thickness iteratively but requires measurements of the electron dose and knowledge of the mass-absorption coefficients.

The method developed recently by us [4-7] does not need any of those external factors (thickness, density, mass-thickness) of the sample to be measured but relies on using a measured K/L intensity ratio as an internal absorption reference. In the following, we apply this to thin layers of $\text{In}_x\text{Ga}_{1-x}\text{N}$.

2. Theoretical considerations

The original Cliff-Lorimer equation uses k -factors for weight% to relate concentrations, c , to measured intensities I , for two elements i and j in a very thin sample section in the form of

$$c_i/c_j = k_{ij} I_i/I_j \quad (\text{equation 1}).$$

The k -factors in this equation are sensitivity factors that depend on the primary voltage, the X-ray fluorescence yield of the corresponding line and the energy-dependence of the sensitivity of the X-ray detector, compared to that of a standard. Only one X-ray line per element must be used to avoid double weightings. Most microscopists use the hardest X-ray line detectable for each element so



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absorption effects are kept minimal. For a multi-component alloy, $\sum c_i = 1$ and with simple relationships such as identity ($k_{ii} = 1$), inversion ($k_{ij} = k_{ji}^{-1}$) and transferability ($k_{ij} = k_{i,Si} \times k_{Si,j}$) it can be shown that weight fractions are given by

$$c_i = \frac{I_i k_{i,Si}}{\sum_j I_j k_{j,Si}} \quad (\text{equation 2})$$

and atomic concentrations by

$$x_i = \frac{I_i k_{i,Si} / A_i}{\sum_j I_j k_{j,Si} / A_j} \quad (\text{equation 3})$$

where A_j denotes the atomic weight of element j . Considering a ternary semiconductor alloy such as $\text{In}_x\text{Ga}_{1-x}\text{N}$ where the group-V sub-lattice is fixed we get for the group-III sub-lattice

$$x = \frac{I_{In} k_{In,Si} / A_{In}}{I_{In} k_{In,Si} / A_{In} + I_{Ga} k_{Ga,Si} / A_{Ga}} = \frac{I_{In} k_{In,Ga}}{I_{In} k_{In,Ga} + I_{Ga} A_{In} / A_{Ga}} \quad (\text{equation 4})$$

and from this

$$k_{In,Ga} = \frac{I_{Ga} A_{In}}{I_{In} A_{Ga} k_{In,Ga}} \times \frac{x}{1-x} \quad (\text{equation 5})$$

According to Cliff and Lorimer [1] this should only hold for a perfectly thin sample without any absorption; with absorption in a thicker sample exponential attenuation of every X-ray line occurs which is taken into account by including mass-thickness (or density), foil thickness and take-off angle as parameters. If instead we incorporate all these effects into k itself, we get effectively thickness-dependent k^* -factors

$$k^*_{InL,GaL} = x I_{GaL} A_{In} / [(1-x) I_{InL} A_{Ga}] \quad (\text{equation 6a, for Ga L})$$

and

$$k^*_{InL,GaK} = x I_{GaK} A_{In} / [(1-x) I_{InL} A_{Ga}] \quad (\text{equation 6b, for Ga K})$$

that are no longer constant factors but vary, as the intensities measured depend on absorption.

3. Simulations

For InGaN the X-ray lines of relevance are, listed in order of increasing energy in eV: N K (392); Ga L α (1098) and L β (1125); In L α (3287), L β_1 (3487), L β_2 (3714) and L γ_1 (3921); Ga K α (9243) and K β (10264); In K α (24139) and K β (27278). Figure 1 shows Monte Carlo simulations [8] of the dependence of $k^*_{InL,Ga}$ vs. Ga K/L ratio for $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys of different indium concentrations. Curves for $x > 0.5$ almost overlap, but for lower indium concentrations they differ, hence, no unique calibration curve as in the case of $\text{In}_x\text{Ga}_{1-x}\text{As}$ [6] is obtained. However, all curves are monotonic as a function of Ga K/L ratio (all of them decreasing, due to absorption increasing with foil thickness), do not cross and yield higher $k^*_{InL,Ga}$ values for lower x values. This can be applied to determine the correct indium concentration of an alloy, x , iteratively: from the measured K/L ratio of a spectrum, any simulated calibration curve for x_{in} may be used as a starting point to estimate a value of k^* . Using this and the measured intensities, I , of the In L and Ga L (or In L and Ga K) lines as well as the atomic weights, A , a first estimate of x_{out} is obtained using equation (4). If $x_{out} > [<] x_{in}$, then the estimate of k^* was too big [small] and a calibration curve for a larger [lower] value of x_{in} must be used, which will yield a lower [higher] k^* value and thus a reduced [increased] x_{out} . Iteration will stop when $x_{out} \approx x_{in}$ at which point the correct indium concentration corresponds to the value of x_{out} for which the best fit simulation is available. The convergence is very quick: usually 2 or 3 iterations suffice. The approximate sign refers to the finite increments for which curves for x_{in} are simulated. In the case of figure 1 we used $\Delta x = 0.2$ and already obtained sufficiently converged x values (with $\Delta x \leq 0.02$ from linear interpolation) after only 2 iterations. This procedure has several advantages over standard absorption corrections:

- a) no estimates of foil thickness, density or mass-thickness are required, as the Ga K/L ratio can be calculated directly for each individual spectrum, serving as an internal standard [5];
 b) results from quantification using the Ga L or the Ga K line are automatically self-consistent [6,7];
 c) the detector sensitivity is no longer critical because the Ga K/L ratio as horizontal axis serves quasi as an internal self-correction, as shown in figure 2 where we simulated, for the example of $x=0.5$, the curves for an ideal detector with constant detection efficiency for all X-ray lines and our Si:Li detector with a thin window [7]. A reduced sensitivity for low energetic X-rays means, firstly, that the Ga K/L ratio will be increased, inducing a shift of all curves to the right. Secondly, as $I_{\text{GaL}} / I_{\text{InL}}$ in equation 6a will be reduced, the monotonically decreasing curve for $k^*_{\text{InL},\text{GaL}}$ will move down vertically so that in effect figure 2a will be almost unchanged. The ratio $I_{\text{GaK}} / I_{\text{InL}}$ in equation 6b will correspondingly increase so that the monotonically increasing curve for $k^*_{\text{InL},\text{GaK}}$ will move upwards vertically and, again, in effect it will be shifted only very little, by ~4% in figure 2b.

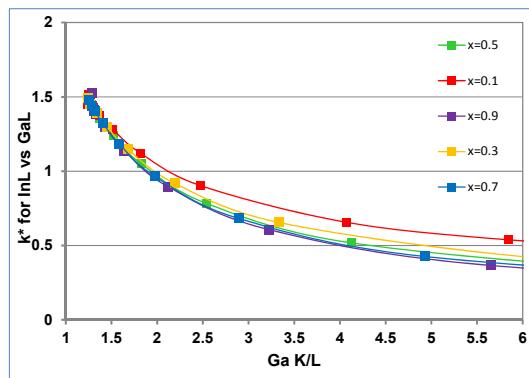


Figure 1a. CASINO simulations of $k^*_{\text{InL},\text{GaL}}$ for $\text{In}_x\text{Ga}_{1-x}\text{N}$, 10^6 electrons, 200kV, 25° take-off angle, $\rho_{\text{GaN}} = 6.15 \text{ g/cm}^3$, $\rho_{\text{InN}} = 6.91 \text{ g/cm}^3$, ideal detector, thicknesses up to ~1500nm ($x=0.1$).

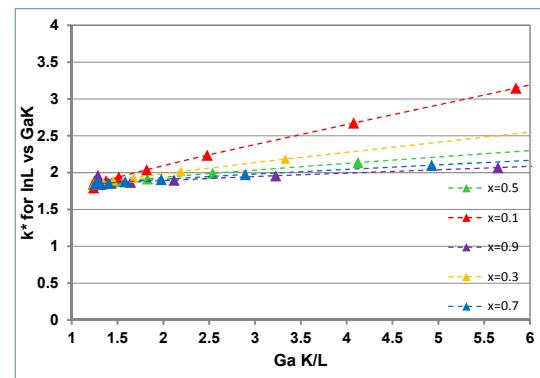


Figure 1b. CASINO simulations of $k^*_{\text{InL},\text{GaK}}$ for various indium concentrations x , rest as for left.

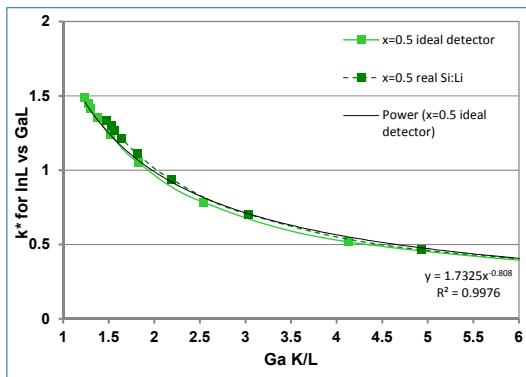


Figure 2a. CASINO simulations of $k^*_{\text{InL},\text{GaL}}$ for $\text{In}_x\text{Ga}_{1-x}\text{N}$ with ideal and Si:Li detector with modelled ratios of detector efficiencies of $\varepsilon_{\text{GaK}}/\varepsilon_{\text{GaL}}=1.196$ and $\varepsilon_{\text{GaL}}/\varepsilon_{\text{InL}}=0.896$.

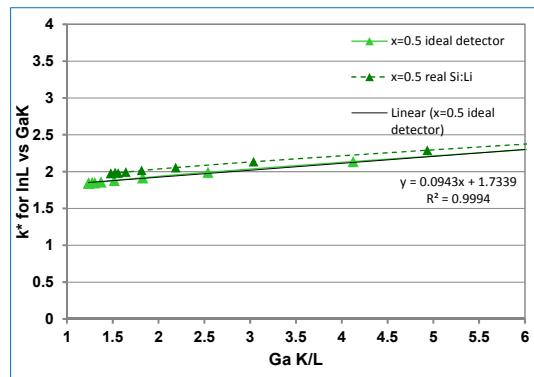


Figure 2b. CASINO simulations for of $k^*_{\text{InL},\text{GaK}}$ for ideal and Si:Li detector with modelled ratios of detector efficiencies of $\varepsilon_{\text{GaK}}/\varepsilon_{\text{GaL}}=1.196$ and $\varepsilon_{\text{GaK}}/\varepsilon_{\text{InL}}=1.072$.

4. Experimental

As a test case, X-ray spectra were recorded from several regions of nine different specimens of InGaN thin layers of differing indium concentrations, deposited on GaN buffers and Al_2O_3 corundum substrates. The experiments were performed using a JEOL 2010F field-emission TEM operated at 197kV and equipped with an Oxford Instruments Si:Li detector with ultrathin Moxtek polymer window and 25° nominal take-off angle. Standard quantification procedures in the Oxford Instruments ISIS300 software yielded inconsistent values using the nominal thin film k -factors for Ga L and Ga K lines (diamonds in figure 3), even after approximate inclusion of absorption corrections (triangles).

Our new quantification scheme suggests indium concentrations are actually higher than the nominal concentrations for low x samples, and quantifications from Ga L and Ga K lines now agree very well for each spectrum. For the averages of our 9 specimens we get as difference between quantification using the Ga L and the Ga K line intensities as reference: $\Delta x = x_{k^* \text{InL,GaL}} - x_{k^* \text{InL,GaK}} = 0.005 \pm 0.007 \leq 0.01$. The error bars of the data in figure 3, where we plot the indium concentration determined using different EDXS method vs the nominal indium concentrations, as given by the scatter from each individual specimen, are significantly larger than above Δx because most samples showed a systematic decrease in apparent x with thickness, indicating indium depleted surface regions. Whether this apparently reduced indium content in the top of the layers is to be attributed to growth, or to argon ion milling, is presently unclear. However, we have excluded beam damage as a cause of this as we tested with a focused electron probe of same intensity that beam damage in the form of preferential loss of indium occurs only after a dose typically factors 20-50 above that used for the measurements shown in figure 3 [7]. For the eight specimens of higher indium concentrations measured in figure 3 it can be seen that the EDXS results from our k^* method lie between those values reported by the ISIS software without any absorption corrections using either Ga L or K lines but are generally closer to those results for Ga L than with Ga K quantification, so neither simple averaging of reported ISIS values nor absorption correction in ISIS will give similar improvements. The first data points for the measurement of the sample with the lowest indium concentration show a different trend, where ISIS and our values have negligible statistical error bars but do not overlap. We are presently testing whether this apparent outlier is due to chemical inhomogeneity of this specific sample.

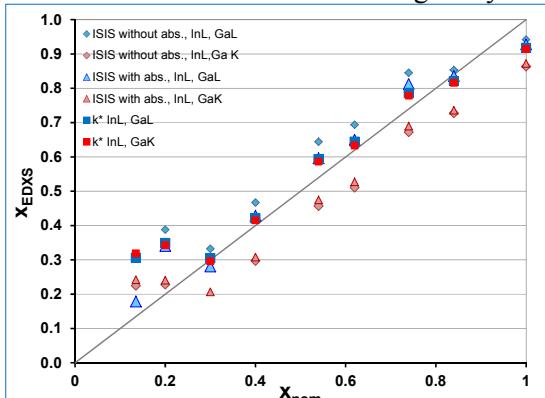


Figure 3: Indium concentration measured by ISIS and our iterative method using k^* values from figure 1.

5. Summary

A new self-consistent absorption correction has been tested on a series of $\text{In}_x\text{Ga}_{1-x}\text{N}$ thin layers of various concentrations x , for which standard quantification procedures yielded inconsistent values using nominal k -factors for Ga L and Ga K lines, even after inclusion of absorption corrections. Our new quantification scheme suggests indium concentrations are actually higher than the nominal concentrations for low x samples. Quantifications from Ga L and Ga K lines now agree to typically better than $\Delta x \leq 0.01 = 1\text{at\%}$ for each spectrum. Total errors are larger because our samples showed an apparent decrease in x with sample thickness, indicating indium depleted surface regions.

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