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Self-consistent method for quantifying indium content from X-ray spectra of thick compound semiconductor specimens in a transmission electron microscope

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Key words. Absorption correction, analytical TEM, InGaN, X-ray spectroscopy.

Summary

Based on Monte Carlo simulations of X-ray generation by fast electrons we calculate curves of effective sensitivity factors for analytical transmission electron microscopy based energy-dispersive X-ray spectroscopy including absorption and fluorescence effects, as a function of Ga K/L ratio for different indium and gallium containing compound semiconductors. For the case of InGaN alloy thin films we show that experimental spectra can thus be quantified without the need to measure specimen thickness or density, yielding self-consistent values for quantification with Ga K and Ga L lines. The effect of uncertainties in the detector efficiency are also shown to be reduced.

Introduction

Energy-dispersive X-ray spectroscopy is a routine method to perform qualitative local chemical analysis of cross-sectioned samples in a transmission electron microscope. For thin specimens, absorption and fluorescence effects may be ignored and the standard Cliff-Lorimer *k*-factor approach can be used (Cliff & Lorimer, 1975) to determine the chemical composition also quantitatively in cross-section. Simply averaging experimental results from near-edge regions of thinned reference specimens of know compositions raises two critical questions:

(1) When can a specimen be considered sufficiently thin?
(2) Will surface effects influence the results for very thin specimens?

The answer to question (1) will depend on the accuracy needed, which itself may be difficult to estimate. An answer to question (2) will have to consider both specimen preparation artefacts, such as surface amorphization and possible indium droplet formation on the surfaces of In containing compound semiconductors, as well as postpreparation chemically selective surface oxidation of cross-sectioned lamellae, which tends to be a problem for many semiconductors that form 1 to 2 nm of amorphous oxides almost instantly when exposed to air (Walther *et al.*, 1995; Walther & Humphreys, 1997) for direct imaging of these surface layers.

For thick specimens, the thin film approach does no longer work, and quantification typically relies on a number of approximations to model absorption and fluorescence within the specimen and the detector efficiency of the individual X-ray lines. Estimates of foil thickness and density are usually required for the absorption correction; alternatively mass absorption coefficient, beam current and specimen density need to be known (Williams & Carter, 1996). The thickness of the specimen can be quite difficult to measure experimentally, and if one knew the density precisely in advance then for a ternary semiconductor (quasi-binary compound if one sub-lattice is kept fixed) the chemistry would be directly related. In particular, the zeta-factor method (Watanabe *et al.*, 1996) developed as an alternative to the Cliff–Lorimer method also does not need the specimen thickness but still requires the mass absorption coefficients and that spectral standards be recorded at constant beam current density.

Here, theoretical and experimental results from InGaN are compared, and a self-consistent scheme is described whereby a thickness-dependent, effective *k*-factor, denoted k^*, can be directly determined from the K/L intensity ratio of at least one of the constituting elements. This makes thickness or density estimates for absorption and fluorescence correction no longer necessary, does not require beam current monitoring, and provides a self-calibrating quantification that is consistent whether *k*-factors of the In L line relative to Ga K or to Ga L are used.

Definition of effective *k*-factors, k^*

For InGaAs or InGaSb, the heavy element of the group-V sublattice (arsenic or antimony) can be used for reference

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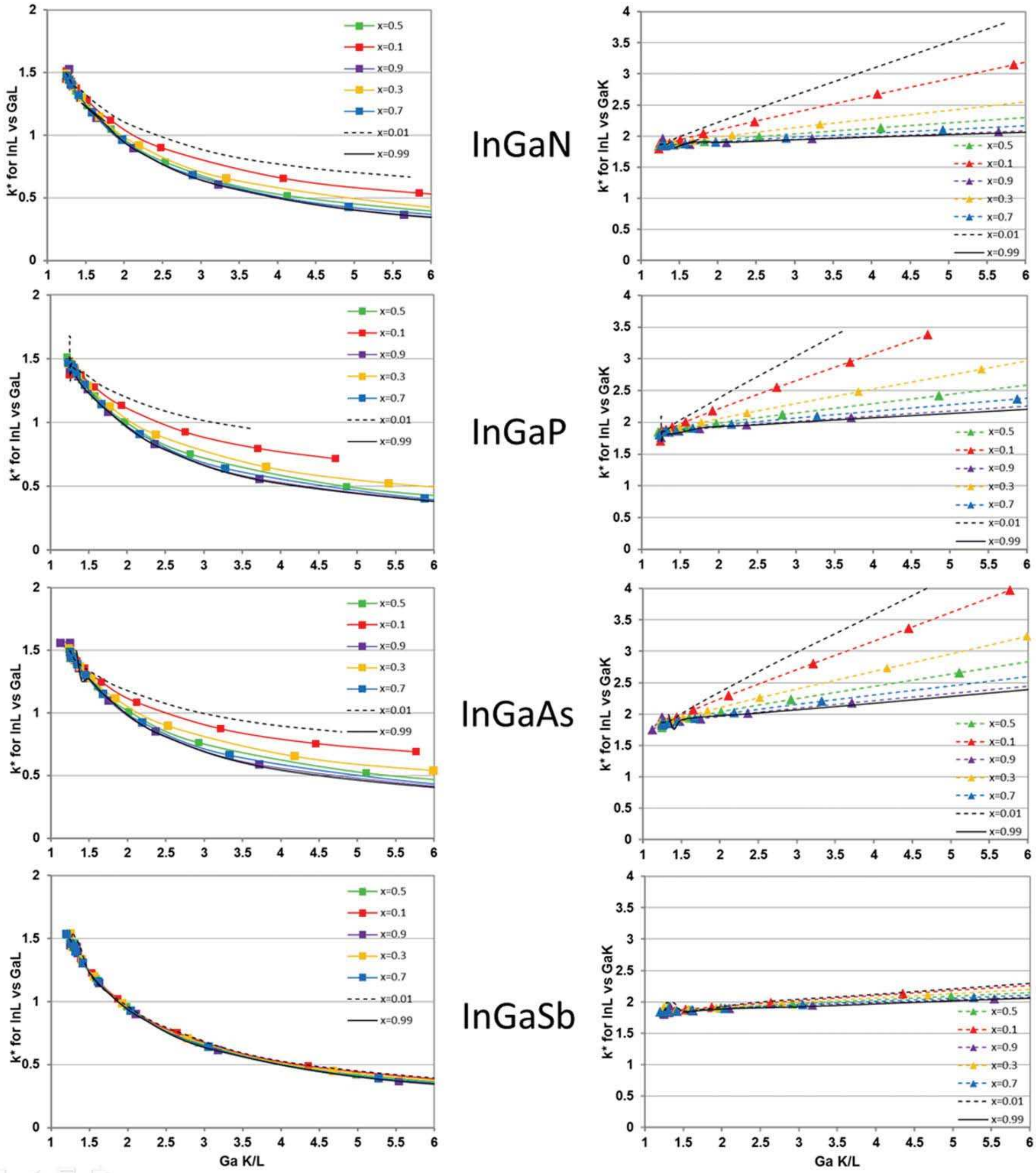

Fig. 1. CASINO simulations of $k^*_{\mathrm{InL,GaL}}$ (left column) and $k^*_{\mathrm{InL,GaK}}$ (right column) for different alloys with different indium concentrations x. Rows are for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ (top), $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$, $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$, and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{Sb}$ (bottom) for one million electrons, 200 kV, 25° take-off angle, ideal detector (equal detection probability for all X-rays), densities interpolated linearly between those of the corresponding binary compounds. The diagrams in each column are drawn to the same scale.

of a known concentration (50%), and it has recently been shown that plots of an effective *k*-factor, $k^*_{\mathrm{In,As}}$, as function of As K/L ratio yield unique calibration curves that can provide the indium concentration in a precise and self-consistent way for InGaAs using the As L or the As K line as reference (Parri *et al.*, 2015).

Nitrogen has no L line and so for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ alloys only the Ga X-ray lines can serve as reference. The same in principle applies to InGaP, where phosphorus has only very weak and low-energy L lines (0.13–0.18 keV) that are difficult to detect and almost impossible to quantify, even for a windowless X-ray detector. The corresponding effective *k*-factors of the indium L line with respect to the gallium K or L lines would be given for all of the above four compounds, InGaN, InGaP, InGaAs and InGaSb, by

$$k^*_{\mathrm{InL,GaL}} = x\, I_{\mathrm{GaL}}\, A_{\mathrm{In}} / [(1-x)\, I_{\mathrm{InL}}\, A_{\mathrm{Ga}}]$$

(equation 1a, for Ga L)

and

$$k^*_{\mathrm{InL,GaK}} = x\, I_{\mathrm{GaK}}\, A_{\mathrm{In}} / [(1-x)\, I_{\mathrm{InL}}\, A_{\mathrm{Ga}}]$$

(equation 1b, for Ga K) ,

where *k* is the *k*-factor for weight percentages, *x* denotes the indium fraction of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{V}$ (V = group-V element), *A* is the atomic weight of an element and *I* the net intensity of its characteristic X-ray line.

Monte Carlo simulations for InGaN, InGaP, InGaAs and InGaSb

Figure 1 shows Monte Carlo simulations of the dependence of $k^*_{\mathrm{In,Ga}}$ versus Ga K/L ratio for $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$, $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{P}$, $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{Sb}$ alloys of different indium concentrations, calculated for 1 million 200 keV primary electrons, an ideal detector at 25° take-off angle and a dozen different thicknesses of 2, 4, 8, 16, 32, 64, 128, 256, 500, 1000, 1500 and 2000 nm.

We used the CASINO code, version 2.42 (Hovington *et al.*, 1997) with interpolated Mott scattering cross-sections (Drouin *et al.*, 1997), ionization cross-sections by Casnati *et al.*, (1982) and empirical stopping power data by Joy and Luo (1989). For the trends observed and discussed here, the exact parametrization should, however, not be critical as, first, concentrations and *k*-factors are functions of intensity ratios rather than absolute intensities and, second, we are concerned mainly with absorption effects, that is the change of the above ratios with specimen thickness.

The form of all sets of curves is very similar, describing an exponential drop of $k^*_{\mathrm{InL,GaL}}$ as the In L line is less strongly absorbed than the reference Ga L line and a slight exponential, almost linear, increase of $k^*_{\mathrm{InL,GaK}}$ as the In L line is more strongly absorbed than the hard Ga K line. The latter is different for the case of SiGe (Qiu *et al.*, 2013) where the $k^*_{\mathrm{GeL,SiK}}$ actually also decreased, very similar to $k^*_{\mathrm{GeK,SiK}}$, which indicates strong fluorescence from Si K to Ge L line.

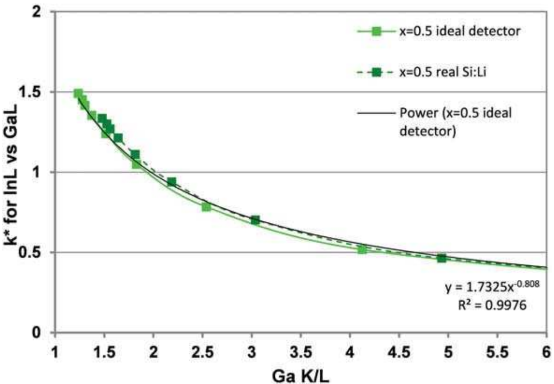

Fig. 2. CASINO simulations for of $k^*_{\mathrm{InL,GaL}}$ for ideal and real Si:Li detector with modelled ratios of detector efficiencies of $\varepsilon_{\mathrm{GaK}}/\varepsilon_{\mathrm{GaL}} = 1.196$ and $\varepsilon_{\mathrm{GaL}}/\varepsilon_{\mathrm{InL}} = 0.896$. One million electrons, 200 kV, 25° take-off angle, $\rho = 6.15\ \mathrm{g\ cm^{-3}}$ for GaN and $6.91\ \mathrm{g\ cm^{-3}}$ for InN.

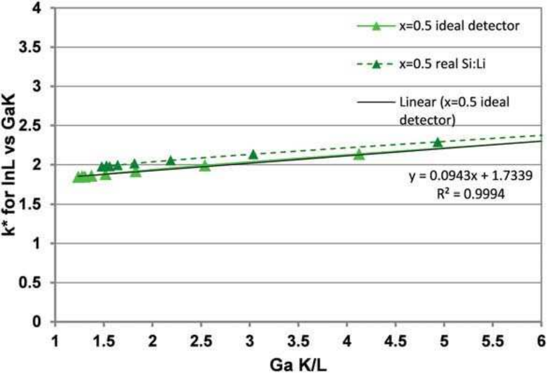

Fig. 3. CASINO simulations for of $k^*_{\mathrm{InL,GaK}}$ for ideal and real Si:Li detector with modelled ratios of detector efficiencies of $\varepsilon_{\mathrm{GaK}}/\varepsilon_{\mathrm{GaL}} = 1.196$ and $\varepsilon_{\mathrm{GaK}}/\varepsilon_{\mathrm{InL}} = 1.072$.

For the specimens considered here fluorescence effects seem to be much weaker. It is clear that here the simulated curves for $x > 0.5$ almost overlap (for InGaSb almost perfectly), but for lower indium concentrations they differ significantly; hence, no unique calibration curve is obtained. However, all curves are monotonic as a function of Ga K/L ratio, do not overlap or cross and yield higher $k^*_{\mathrm{In,Ga}}$ values for lower *x* values.

It is also important to point out that although the above simulations have been performed for an ideal detector, they will hardly change if a realistic detector performance is included, as shown explicitly in Figures 2 and 3 for the example of an $\mathrm{In}_{0.5}\mathrm{Ga}_{0.5}\mathrm{N}$ thin film and the Si:Li detector used in our experimental study. This is due to the detector sensitivity influencing the scale of both axes in such a way that the calibration curves hardly move at all (by about 4% relative in Fig. 3, which would be difficult to measure experimentally).

Proposal of an iterative method to determine indium content

The above simulations can be used to determine the correct indium concentration of an alloy, *x*, in an iterative scheme: from the measured Ga 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*, of the elements, a first estimate of x_{out} is obtained using the relationship

$$x_{out,L} = I_{InL}k^*_{InL,GaL}/\left(I_{InL}k^*_{InL,GaL} + I_{GaL}A_{In}/A_{Ga}\right)$$

(equation 2a, for Ga L)

and

$$x_{out,K} = I_{InL}k^*_{InL,GaK}/\left(I_{InL}k^*_{InL,GaK} + I_{GaK}A_{In}/A_{Ga}\right)$$

(equation 2b, for Ga K).

If $x_{out} = x_{in}$, then the correct indium concentration has already been identified. If $x_{out} > x_{in}$, then the estimate of *k** was too big and a calibration curve for a larger value of x_{in} must be used, which will yield a lower *k** value and thus a reduced x_{out}. If $x_{out} < x_{in}$, then the estimate of *k** was too small and a calibration curve for a lower value of x_{in} must be used, which will yield a larger *k** value and thus an 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 two or three iterations suffice. The approximate sign refers to the finite increments for which curves for x_{in} have been simulated. In the case of Figure 1 we used $\Delta x \sim 0.2$ and already obtained sufficiently converged *x* values ($\Delta x \leq 0.02$) by interpolation after only one or two iterations.

This procedure has several advantages over standard absorption corrections:

(1) no estimates of foil thickness or density are required, and the Ga K/L ratio can be directly read out for each individual spectrum;

(2) results from quantification using either the Ga L or the Ga K line are self-consistent;

(3) the detector sensitivity is not an issue because the Ga K/L ratio as horizontal axis serves quasi as an internal self-correction. In Figures 2 and 3 we have simulated, for the example of $x = 0.5$, the curves for an ideal detector and a typical Si : Li detector with ultrathin window as used in our laboratory. A reduced sensitivity for lower energetic X-rays means, first, that the Ga K/L ratio will be increased, introducing a shift to the right. Second, as I_{GaL}/I_{InL} in Eq. (1a) will be reduced, the monotonically decreasing curve for $k^*_{InL,GaL}$ will move down vertically so that in effect it will be almost unchanged (cf. Fig. 2). The ratio I_{GaK}/I_{InL} in Eq. (1b) will be correspondingly increased so that the monotonically increasing curve for $k^*_{InL,GaK}$ will move upwards vertically and, again, in effect it will be shifted only very little, by about 4% for $x = 0.5$ (cf. Fig. 3), yielding a systematic overestimate of $\Delta x = 0.02$ in the worst case.

Experiments for InGaN

This self-consistent absorption correction should improve quantification. As a test case, X-ray spectra were recorded from several regions of nine different specimens of InGaN thin layers of differing nominal indium concentrations, estimated from the growth parameters and, for the layers of higher indium content, confirmed by X-ray diffraction. These layers were deposited on GaN buffers and Al_2O_3 corundum substrates.

Cross-sectional specimens for TEM studies were prepared by cutting, grinding and dimpling, followed by ion milling. In order to minimise ion beam damage, the samples were maintained at liquid nitrogen temperature during ion milling using a Gatan PIPS at 5 keV, with a final polishing step at 0.6 keV. The incident beam angle was kept at 5° for both guns. Some of the samples were stored in sample boxes for over a year, leading to some surface oxidation.

The experiments were performed using our JEOL 2010F field-emission transmission electron microscope operated at 197 kV. It is equipped with an Oxford Instruments Link Pentafet 30 mm^2 Si : Li detector (model 6498) with a ~300 nm thin polymer window (ATW2 type) and gives 25° nominal take-off angle for an untilted specimen holder, achieving 136 eV energy resolution at 5.9 keV (Mn Kα line). The standard quantification procedures in the Oxford Instruments ISIS300 software were used to separate the characteristic X-ray peaks from the Bremsstrahlung background and integrate their net intensities but yielded inconsistent values using the nominal thin film *k*-factors for Ga L and Ga K lines (shown as diamonds in Fig. 4), even after approximate inclusion of absorption corrections (not shown). Our new quantification scheme suggests indium concentrations are actually higher than the nominal concentrations for low *x*, and quantification from Ga L and Ga K lines now agrees very well for each spectrum. For the averages of our nine specimens we get for the difference between quantification using the Ga L and the Ga K line intensities as reference: $Dx = x^*_{k\,InL,GaL} - x^*_{k\,InL,GaK} = 0.005 \pm 0.007 < 0.01$.

The error bars reported in Figure 4, where we plot the indium concentration determined using the above iterative EDXS method versus the nominal indium concentrations, refer to the scatter for each specimen, which is significantly larger because our samples showed a systematic decrease in apparent *x* with thickness, indicating indium depleted surface regions. Whether this apparently reduced indium concentration in the top of the layers is to be attributed to growth or to specimen preparation by argon ion milling, is presently unclear. However, we can exclude beam damage as a possible cause of this as we have tested with a focused electron probe

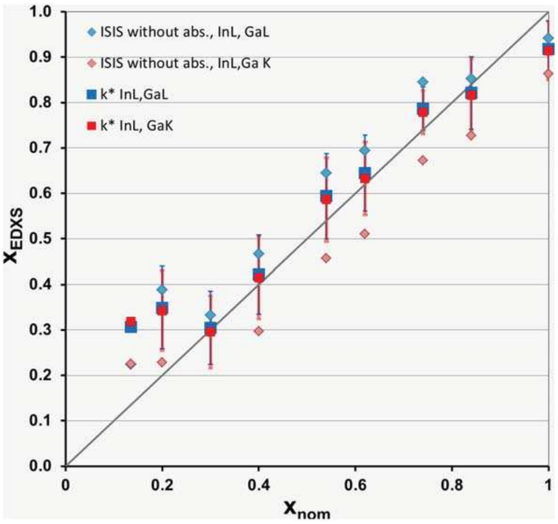

Fig. 4. Indium concentration measured by our iterative method using the calibrated k^* values from the top row of Figure 1, plotted as function of the nominal concentrations.

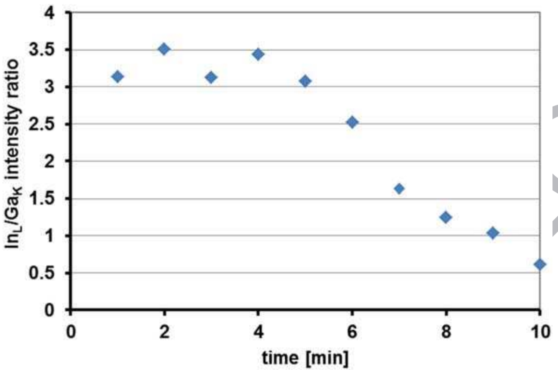

Fig. 5. Measured In/Ga ratio for the $In_{0.63}Ga_{0.37}N$ specimen with beam focused to ~10-nm diameter. Preferential sputtering of In occurs after ~5 minutes, corresponding to a dose of 2×10^6 C cm^{-2}. We typically stayed factors 20–50 below that threshold for the measurements shown in Figure 4.

of same intensity (~5 nA, ~10 nm diameter instead of the ≥ 50 nm diameter used for the above series of measurements) that beam damage in the form of preferential loss of indium by sputtering occurs only after a dose typically factors 20–50 above that used for the measurements shown in Figure 4.

Figure 5 shows a time series of such X-ray spectra acquired from one position on the $In_{0.63}Ga_{0.37}N$ specimen with a nano-probe, where after ~5 min (corresponding to a dose of ~2×10^6 C cm^{-2}) the measured In/Ga ratio starts to decrease systematically, indicating preferential indium loss from the specimen.

In Figure 4 it can be seen that for measurements from eight specimens, the EDXS results from our method lie between those values reported by the ISIS software without any absorption corrections: generally, values from k^* are closer to those ISIS values with Ga L (which lie $\Delta x = 0.041$ above) than with Ga K quantification (which lie $\Delta x = -0.091$ below the x values from k^*), so simply averaging both quantification options from ISIS would give values systematically lower than from our new k^* approach by about -0.025. If we included an approximate absorption correction in ISIS (assuming a linear correlation between count rate and thickness and assuming the later rises to up to 600 nm) then the ISIS values for quantification based on the Ga L line would move towards our quantification based on $k^*_{\mathrm{InL,GaL}}$, whereas the quantification based on the Ga K line would remain almost unchanged. As a result, the spread would be reduced somewhat but averaging absorption corrected results from both L and K lines would move the averaged data into the wrong direction, giving an even larger underestimate of -0.04. The first data points for the measurement of the InGaN specimen with the nominally lowest indium concentration show a significantly different trend, where ISIS and our values have almost negligible individual measurement errors but their error bars do not overlap. We are therefore presently considering to extend the study to more specimens of lower indium concentration to check the origin of this outlier. It can further be seen that quantification using $k^*_{\mathrm{InL,GaL}}$ or $k^*_{\mathrm{InL,GaK}}$ give almost identical results, to within ± 0.006. Remembering that the error bars in Figure 4 refer to the repeatability of quantification from a series of typically four to nine spectra from different positions of different thicknesses from the same specimen, the standard errors of the mean values will be ~~—~~two to three times lower than indicated by error bars in Figure 4.

Conclusion

We have applied the recently proposed concept of thickness-dependent effective k-factors for semiconductor alloys to measurements of the concentration of a series of InGaN specimens from EDXS. By defining an effective k-factor from Monte Carlo simulations that included both absorption and fluorescence effects for the same Ga K/L ratio as experimentally measured, we achieved self-consistent agreement between the quantification using Ga L and Ga K lines. The advantage of this method is that neither specimen thickness nor density of the specimen need be known, as the absorption correction is inherent in the Ga K/L ratio measurement which is readily available from each individual spectrum and serves as inherent calibration. Our method is also shown to be robust to uncertainties in the detector efficiency.

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