Self-consistent absorption corrections for low-energy X-ray lines in energy-dispersive X-ray spectroscopy

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Quantification of energy-dispersive X-ray spectra in transmission electron microscopy is often unreliable for X-ray lines of low energy, as they are subject to strong absorption and fluorescence corrections which will depend critically on both the sample thickness and the detector properties (take-off angle, detector material and type, thickness and cleanliness of any detector window). By using the method to vary the take-off angle between repeated measurements in energy-dispersive X-ray spectroscopy from the same region, an attempt has been made to study our ability to determine the depth of a buried epitaxial thin layer within a plan-view sample and to correctly assess the composition of specimens containing lighter elements. By using several different Monte Carlo simulation programs, the attenuation of the X-rays along their path towards the detector can be calculated and the predicted results can be compared to experimental measurements. Comparison of two different programs to experimental results has been made, for an InAs quantum well buried beneath a GaAs cap layer and a NiO thin film specimen.

1. Introduction
Attempting to use energy dispersive X-ray spectroscopy (EDXS) for quantification using low energy X-rays is often unreliable. Since the intensity of such low energy radiation is strongly susceptible to various factors, such as the type of the detector and in particular its entrance window, acquiring data for a useful absorption correction is experimentally difficult. As such, Monte Carlo simulation programs have been used in an attempt to calculate this information.

Further, a method for calculating the depth of a layer within another material or the thickness along the beam direction of a homogenous sample has been described. If expanded, this method could be used as verification of other techniques, such as depth-profiling by secondary ion-mass spectroscopy or scanning Auger spectroscopy, allowing for greater accuracy in their depth calibration.

2. Monte Carlo program comparison for absorption
Building upon previous work [1], four Monte Carlo simulation programs will be compared for their ability to accurately model X-ray absorption. This has been done by simulating X-ray generation and absorption in a gallium arsenide sample of varying thickness and calculating the ratio of the As K-line to the As L-line intensity.

Figure 1 is a plot of these curves on a logarithmic scale, along with experimental measurements from a cleaved GaAs wedge sample. All four programs show similar curves (though EDAX Electron Flight Simulator [2] has a hard coded limitation prohibiting it from calculating values for t>3μm), however, there is considerable shift between these curves.
Recalling that no detector is perfectly efficient, it is clear that taking the ratio of two X-ray intensities of different energies would have to include a correction factor, since both lines, depending on the precise energies involved, may not be detected with the same efficiency. As a first order approximation, a typical efficiency graph [3] implies that a Si:Li detector with atmospheric thin window would detect As\(_{L}\) at between 60 and 80\% while As\(_{K}\) at ~100\% efficiency. As such, the experimental results should be corrected by this factor so as to be comparable to the simulated data, however this correction is negligible on a logarithmic scale. As an approximate compromise, this efficiency has been presumed to be 70\%, and the experimental data in figure 1 adjusted accordingly.

![Graph](image)

**Figure 1:** As\(_{K}\) to As\(_{L}\) ratio comparison for four programs and experimental data from a cleaved GaAs wedge for primary energy of 197kV and an approximate take-off angle for flat samples of 20°.

### 3. Depth of an InGaAs single quantum well buried in an InAs/GaAs specimen

The existing method of calculating the depth of a layer in a thin foil [7] has proved to be very sensitive to noise and inconsistencies in the sample position and thickness. An alternative method has been developed, that is somewhat more insensitive to noise.

Recalling that X-rays of different energies are absorbed differently, normalising an X-ray intensity of a certain energy with respect to another at a different energy will provide information about the sample if the take-off angle (and therefore the effective thickness) is varied. This can then be compared to previously calculated standards.

Using indium in gallium arsenide as an example, taking the intensity ratio of In\(_{L}\) (3.287keV) over As\(_{L}\) (1.282keV) and In\(_{L}\) over As\(_{K}\) (10.543keV) gives two ratios with different dependences on sample thickness and hence take-off angle. The ratio In\(_{L}\) / As\(_{L}\), since As\(_{L}\) is more heavily absorbed even considering self-fluorescence, will decrease as the take-off angle increases, while In\(_{L}\) / As\(_{K}\) will increase with take-off angle. In theory, these two ratio curves can be matched to data from simulations. The data presented below was gathered with a nominal take-off angle of \(\theta=25°\) and a solid-angle of detection of 0.12srad and specimen tilt \(\alpha\) where \(\alpha>0\) means tilt towards the detector.

Figure 3 shows these ratios for two regions of nominally identical GaAs samples with an 8nm thick In\(_{0.24}\)Ga\(_{0.76}\)As layer under a GaAs cap of 95nm, in agreement with annular dark-field scanning TEM in cross-section, as shown in figure 2. Using the As\(_{K}\) / As\(_{L}\) ratio at \(\alpha=0°\) specimen tilt gave 2.60 and 2.99 for the first and second sample, respectively. While this data was collected with a take-off angle of 25° instead of 20° the difference seemed small enough to vanish into the error. These values were then
compared to the CASINO and NISTMonte plots from figure 1 and the calculated total thickness was then read off the x axis. This resulted in a thickness estimate of 236nm (Casino) to 424nm (NISTMonte) for the first sample and 276 to 546nm for the second, respectively. The degree of scatter is considerable, but a clear trend in agreement with the above described expectation is observed in the In$_{L}$/As$_{L}$ ratio curve for the second sample. The two In$_{L}$/As$_{K}$ ratio plots (open data symbols) are flatter because both In$_{L}$ and As$_{K}$ are much less absorbed than As$_{L}$.

For a depth $d$ below the surface an X-ray intensity decays exponentially with an absorption length $\lambda_i$ such that $I_i(d) = I_{oi} \exp(-d*/\lambda_i)$, where $d* = d / \sin(\theta + \alpha)$. Then the logarithm of a ratio of two X-ray lines $i = 1,2$ is given by $\log I_1/I_2 = -d*/(\lambda_1 + \lambda_2) + \log I_{o1}/I_{o2}$, which is a linear function of $d*$ with slope $m = -1/(\lambda_1 + \lambda_2)$ and $y$-intercept $b = \log I_{o1}/I_{o2}$.

Calculating the slopes and $y$-intercepts of In$_{L}$/As$_{L}$ and In$_{L}$/As$_{K}$ ratios, as provided by MS Excel 2007’s LOGEST function, and comparing them for equivalent data from simulations conducted by NISTMonte and CASINO, which figure 1 indicated to be the simulation programs that seem to be able to predict K/L line ratios most reliably, does not give readily interpretable results, as seen in figures 4 and 5. These results are for the first sample, with total sample thickness of 236nm from CASINO and 424nm from NISTMonte, as described above. The second sample gives similar data. The $y$-intercept is not strongly dependent on the InGaAs layer’s depth, and the size of the error bars precludes using it for an accurate comparison. The slope evaluation of the NISTMonte In$_{L}$/As$_{L}$ plot from figure 4 would...
indicate that the layer must be buried at a depth somewhere between 1 and 160nm, while the CASINO data do not match at all.

The reasons for the discrepancy between the experimental and the simulated results are not clear. Most obviously, the simulations included a perfect detector, without any loss of efficiency along the energy spectrum, whereas the experiment uses a Si (Li) detector with a polymer thin window capable of withstanding the pressure from the evacuated column. Such reduced detector efficiency would cause a change in the absolute values but not of the curvature, and should not be of great concern.

4. Chemical composition of a NiO bulk test specimen

A comparison between a nominal 58nm thick NiO bulk sample and NISTMonte simulations of different thicknesses was carried out. This comparison involved the Ni K (7.478keV), Ni L (0.851keV) and O K (0.525keV) lines. Figure 6 displays the experimental results. The Ni K / Ni L and Ni K / O K intensity ratios decrease with increasing tilt, as expected, while the Ni L / O K ratio remains almost constant. Both of these trends agree with theory.

Figure 7 shows fits to the simulated and experimental results. Both the Ni K / Ni L and the Ni K / O K lines show increasing negative slope with increasing thickness, while the Ni L / O K ratio stays relatively constant: given their similar line energies, this is not a surprise. The numerical discrepancy between experiment and simulation is obvious: the O K-counts decrease faster than the NISTMonte simulations suggest. This difference is likely due to incorrect absorption correction in NISTMonte, rather than e.g. build-up of ice on the detector window, which would have decreased the Ni L-edge intensity similarly. This was not observed.

5. Conclusions

The Casino and NISTMonte codes seem to reproduce experimental ratios of K/L line intensities more accurately than the Hurricane and EDAX Electron Flight Simulator codes.

The qualitative agreement between these codes and theory is good and the depth of a buried thin layer within a sample and the average chemical composition of a thinned bulk sample can be determined to some degree, however, for highly precise measurements almost noiseless experimental spectra will be needed.

References

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