Quantification of series of X-ray spectra taken at different tilts in analytical transmission electron microscopy

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Abstract. In 2007, it was suggested that by varying the take-off angle between repeated measurements of the same region in energy-dispersive X-ray spectroscopy (EDXS) in a transmission electron microscope (TEM) a significant improvement of the accuracy of X-ray quantification could be achieved. Simultaneously, an analytical expression of the depth within the thin foil specimen of the feature analysed was derived, which in turn could be used to better quantify the material of interest. Simulated results for the absorption of a variety of X-rays in different semiconductor substrates using different Monte Carlo programs will be presented, specifically regarding a model which corrects for tilting the specimen toward or away from the detector: a common method of varying the take-off angle. A set of experimental EDX spectra of capped InAs quantum wells or dots taken in plan-view geometry by tilting the specimen holder will be used for comparison of experimental with the simulated data.

1. Explanation of principle
An accurate quantification of a sample from EDX data can be heavily dependent on absorption correction, particularly for the softer (i.e. lower energy) X-rays. This correction is typically achieved by estimating the thickness and density of the material between the source of these X-rays and the detector. By comparing the detected intensities of various X-ray lines to the expected intensity, one can attempt to deduce the reduction in intensity caused by absorption and hence correct for it. However, this approach is not very accurate and often leads to substantial error margins.

A method for calculating the depth of a layer was presented in 2007[1]: one takes multiple readings of the same area under the same conditions except that the take-off angle is varied. This introduces an artificial change in the effective depth of the layer, allowing one to deduce the thickness of the intervening material and therefore quantify the material with potentially greater accuracy.

The correct relationship for calculating this depth, \( d \), is given as equation (1). \( \lambda \) is the attenuation wavelength, \( I \) is the detected intensity and \( \theta \) is the take-off angle:

\[
d = \frac{\lambda \ln \left(\frac{I_1}{I_2}\right) (\cos(\theta_1 - \theta_2) - \cos(\theta_1 + \theta_2))}{4 \sin \left(\frac{\theta_1 - \theta_2}{2}\right) \cos \left(\frac{\theta_1 + \theta_2}{2}\right)}
\]

(1)
2. Methods of calculating the attenuation wavelength

Briefly, the characteristic absorption wavelength is calculated by acquiring or simulating a logarithmic plot of intensity vs. depth of overlayer and applying linear regression to the result. However, creating a sample for each data point, each with different overlayer thickness, is resource intensive and hence not feasible experimentally.

This technique, 'depth variation', as sketched in figure 1, must also take into account beam straggling, as this causes the quantity of generated X-rays to increase the deeper the layer of interest. An accurate result requires either correction for this changing initial intensity (which is feasible in simulations but impossible in a practical experiment) or a high enough beam energy in practice such that the decrease in beam energy in the specimen foil is inconsequential.

By considering the conditions under which characteristic absorption wavelength can be calculated (i.e. change in depth and ergo X-ray intensity) it is clear that by moving the detector (and changing the effective depth) an entire series can be acquired from a single sample. This method, 'detector tilt', figure 2, is simply the realisation of the theoretical approach, and as such does not require a stopping power correction.

Unfortunately, many microscopes do not allow for the X-ray detector to be moved: in these changing the take-off angle is done by tilting the specimen, which itself presents a problem. As the sample tilts from the horizontal, the path taken by the downwards-travelling electrons will pass through a greater quantity of the material, thereby exciting more X-rays. Given that X-rays are produced in roughly linear proportion to the thickness of the material travelled through, trigonometry dictates that the intensity can be reduced to the equivalent of the horizontal set-up while retaining the increased effective depth presented by the specimen tilt. Hence, multiplying the detected intensity by the cosine of the tilt angle of the specimen from the horizontal causes the system to appear as the 'detector tilt' example, allowing the same equation to be used. This can be seen in figure 3.

![Figure 1: Depth variation method. Notice \( \theta = 90^\circ \) take-off angle.](image1)

![Figure 2: Detector tilt method](image2)

![Figure 3: Specimen tilt method](image3)

To demonstrate the facility of the methods described in section 2, a series of simulations were run in NISTMonte[2] where the geometry was manipulated so as to model the three situations. All three simulations were designed such that they were functionally identical. In summary, the samples consisted of 140nm of GaAs (density 5.316 g/cm\(^3\)), within which was embedded 5nm of InAs (density 5.67 g/cm\(^3\)), with a beam energy of 200keV. In the first ('depth variation') the take-off angle was held at 90\(^\circ\) and the depth of the layer varied through \(d=125.6, 95.0, 76.9, 65.0, 56.7, 50.6, 46.0\) and 42.4 nm. The detector tilt method used the InAs layer at \(d=30\)nm deep and the detector was moved to 15, 20, 25, 30, 35, 40, 45 and 50\(^\circ\): at 30nm and 45\(^\circ\), this gives the same effective depth as the first method. For the specimen tilt, the layer was again held at 30nm depth but the specimen tilted through \(\theta=-10, -5, 0, 5, 10, 15, 20\) and 25\(^\circ\), where negative sign means away from the detector: given a typical take-off angle of \(\theta=25^\circ\) this is again equivalent to the first method.
The results of these simulations for the In L-line in GaAs are shown in table 1. It is clear that the depth variable method is far superior in terms of statistical spread of the simulation. Unfortunately, as already mentioned, this method is impractical for experimental work, since neglecting the beam straggling correction would, in this case, throw off the result by up to 9%.

It is worth noting that applying the depth variable correction to the detector tilt method (i.e. dividing detected intensity by generated intensity) improves the error by an order of magnitude, to a similar value as that of the variable depth method.

The specimen tilt method has the worst error, likely due to the correction for the cosine of the tilt angle. Normalising the detected intensity with respect to the generated intensity does not improve the error here. For the specimen tilt, the linear fit was significantly worse than for the other two methods, implying that either the situation causes more data scatter or that the simulation had some minor flaw.

3. Comparison of programs
Table 2 shows the comparison of $\lambda$ between different simulation programs, for increasing energy of the X-ray lines. The ‘depth variation’ technique was used, with $I/I_0$ correction applied, since (as seen above) this has the greatest accuracy of the three methods. It is immediately obvious that the differences are minor for the lower energies but become large for the higher energies, well beyond the stated error. This is due to systematic differences in the models used by the various programs.

Edax Electron Flight Simulator (EEFS) has a low scatter, implying good self-consistency, and yet displays lower calculated values for most lines than the other programs. NISTMonte displays even lower scatter (due to the quality of the linear fit and rounding errors), but shows higher values for all lines. The average value for the In (L) line, 2526nm, was used for the calculations in section 4, since this was the most reasonable value available, although the standard deviation of ±179nm would suggest an error in In$_L$ intensity of approximately 2% at 200nm GaAs thickness.

4. Simulated Data

In Figure 4 the results of three NISTMonte simulations are shown. 4nm of InAs was simulated with a GaAs capping layer of 4nm, 6nm and 8nm thickness. These simulations ignore bremsstrahlung radiation, detector sensitivity and noise. In a real sample this thin, one would expect considerable counting noise.

The data of Figure 4 serve to illustrate that having different thicknesses can

| Line         | NISTMonte | EEFS[3] | Hurricane[4] | Casino[5] |
|--------------|-----------|---------|--------------|-----------|
| N (K)        | 144.2±0.1 | 134.43±0.1 | 140±3        | 138±4     |
| Al (K)       | 365.4±0.1 | 344.62±0.2 | 342±1        | 354±1     |
| Si (K)       | 502.5±0.1 | 418.95±0.3 | 468±10       | 468±1     |
| P (K)        | 725.7±0.1 | 625.88±0.5 | 667±10       | 668±4     |
| In (L)       | 2770.2±0.2 | 2392.64±8.7 | 2390±32     | 2551±2    |
| Sb (L)       | 3627.3±0.3 | 3064.53±11.7 | 3007±42    | 3334±4    |

Table 2: Decay lengths $\lambda$ (nm) for GaAs coverage. Error bars give consistency with exponential function using numerical output from the four different programs.

Figure 4: Results of simulations. Values on the abscissa indicate lower and upper limits of the histogram channels. Note the correct results for depths are the nominal thicknesses of the cap plus ~2nm.
have strong effects, even with such thin material. This conclusion does not hold well for experimental
data, as overcoming counting errors must either be achieved through considerable tilts, limiting the
number of available data points, or long lifetimes, which might cause beam damage during analysis.

5. Experimental data
In this section data from an experimental sample is shown. The sample is an InAs quantum dot layer
on GaAs and has been capped by nominally 6nm GaAs.

There was considerable scatter in the intensity, possibly caused by holes in the capping layer.
Despite this, applying equation (1) to each data point with respect to every other data point gives some
results that appear accurate, in addition to many other results which do not, as seen in figure 5. In this
sample, it was discovered via atomic force microscopy (AFM) that islands had formed, and that the
depth beneath the cap was not a fixed value in this case, however, the mean value may be
approximated by the nominal value of the cap (~6nm) plus half of the InAs thickness (~2nm), i.e.
~8nm. This explains the two peaks indicated by arrows in figure 5.

Those depths that are calculated as negative are the result of $I_1$ being greater than $I_2$ in equation (1),
i.e. the intensity decreased as the sample was tilted towards the detector. This result is inconsistent
with theory and may be due to parallax effects by the sample not being at the correct eucentric height
in the pole-piece anymore when the holder is tilted towards the maximum tilt angles. Negative results
are unphysical and result either from sample inconsistency or large relative error in $I$ (in this case, low
signal to noise ratio).

There are four results which sit within the correct channel (i.e. 6 to 9), with none on either side.
Data at channel 27+ cover a large range (37.5 to 409.4) without any apparent clustering and seem to be
artifacts due to noise that has a particularly strong effect at low take-off angles.

6. Summary
Three different methods of calculating the attenuation wavelength were described and simulated data
used to support their similarity. Four different Monte Carlo programs were used to calculate the
attenuation wavelength and their systematic differences compared. An experimental data set was used
and compared with simulations to test if the method could work experimentally.

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