

Calibration of thickness-dependent k -factors for germanium X-ray lines to improve energy-dispersive X-ray spectroscopy of SiGe layers in analytical transmission electron microscopy

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Abstract. We show that the accuracy of energy-dispersive X-ray spectroscopy can be improved by analysing and comparing multiple lines from the same element. For each line, an effective k -factor can be defined that varies as a function of the intensity ratio of multiple lines (e.g. K/L) from the same element. 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 the specimen thickness itself does not actually need to be measured.

1. Introduction

Energy-dispersive X-ray spectroscopy (EDXS) in a transmission electron microscope (TEM) offers high spatial resolution but usually suffers from both poor counting statistics due to small collection angles and quantification problems due to self-absorption in thin foil specimens analysed under small take-off angles. A first-order approach for quantification is based on experimentally determined sensitivity factors, called k -factors [1]. More accurate quantification of elemental compositions depends on the calculation of the relative ionisation cross-sections of the corresponding elements (Z -effect) [2,3] and 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. While this approximation neglects the top-bottom effect due to the depth of the analysed feature embedded within the thin foil specimen [6], this depth can itself be determined either directly by tilting the specimen through large angles or by means of measuring X-ray intensities as a function of take-off angle during moderate tilting experiments [7] and comparison with corresponding Monte Carlo simulations [8]. It has been shown in previous studies how the conventional thin film approximation for EDXS in a TEM can be improved for a given material system by calibrating k -factors based on linear least-squares fitting X-ray line intensities recorded over a range of sample thicknesses and extrapolation to zero thickness [9,10]. For the AlGaN system such a thickness-extrapolation yielded, together with a minor correction for stray X-rays from the substrate, the local Al content with a precision of $\sim 1\text{at}\%$ [11,12].

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Here, we show that the absolute sample thickness is not necessary for accurate X-ray quantification if several lines are present for at least one element. Our approach is somewhat different from the method described by Morris et al. [13] who suggested to use K/L intensity ratios to first iteratively estimate the sample thickness and from this to perform a correction for fluorescence and absorption for all relevant lines, a procedure which still relies on absolute thickness values.

2. Experimental

If the X-ray intensity of a certain line is compared to that of Si_K as a standard, then the chemical concentration of an element j can be calculated as

$$x_j = (I_j k_{j,\text{Si}_K} a_j / A_j) / (\sum_n I_n k_{n,\text{Si}_K} a_n / A_n) \quad (\text{eqn. 1})$$

where I denotes intensity, k the k -factor with respect to weight %, a the absorption, A the atomic weight and the index n runs over all elements detected. The k -factors in this equation are sensitivity factors that depend on the primary voltage, the X-ray fluorescence yield of the corresponding element and the energy-dependence of the sensitivity of the X-ray detector, compared to that of the standard. The division by atomic weights is only necessary if the k -factors refer to weight % (rather than at%). Suitable k -factors are usually provided by the manufacturer of the EDXS system, and the user has to choose which lines to include in the quantification. It is important that only one X-ray line per element should be used in the above equation, otherwise the result would be distorted by double weightings. Most microscopists use the hardest X-ray line detectable for each element so that absorption effects are as small as possible. Often, absorption in thin foil TEM specimens is neglected ($a_n = 1 \forall n$). For a precise quantification absorption should always be considered, however, the way standard software includes it is only approximate: by assuming a foil of thickness t that is homogeneous in composition along the beam direction. We have developed a method that takes into account all available X-ray lines (K, L etc.) within spectra, thereby performing a self-consistent absorption correction for e.g. K- and L-lines.

We demonstrate this in the following for the SiGe system as an example the results of which have already been applied to quantify the chemical composition of very thin $\text{Si}_{1-x}\text{Ge}_x$ layers [14]. This model system has the advantage that $k_{\text{Si}_K,\text{Si}_K} = a_{\text{Si}_K} = 1$ by definition so that only two further X-ray lines are to be considered: Ge K and Ge L. The K-line is a hard X-ray and shows only very weak absorption, while the L-line is a soft X-ray and heavily absorbed. From above we can derive for the germanium content:

$$x_{\text{Ge}_K} = (I_{\text{Ge}_K} k_{\text{Ge}_K,\text{Si}_K} a_{\text{Ge}_K} / A_{\text{Ge}}) / (I_{\text{Si}} / A_{\text{Si}} + I_{\text{Ge}_K} k_{\text{Ge}_K,\text{Si}_K} a_{\text{Ge}_K} / A_{\text{Ge}}) \quad (\text{eqn. 2}) \quad \text{for the K-line,}$$

$$x_{\text{Ge}_L} = (I_{\text{Ge}_L} k_{\text{Ge}_L,\text{Si}_K} a_{\text{Ge}_L} / A_{\text{Ge}}) / (I_{\text{Si}} / A_{\text{Si}} + I_{\text{Ge}_L} k_{\text{Ge}_L,\text{Si}_K} a_{\text{Ge}_L} / A_{\text{Ge}}) \quad (\text{eqn. 3}) \quad \text{for the L-line.}$$

which *should* be identical ($x_{\text{Ge}_K} = x_{\text{Ge}_L}$) if the k -factors for both lines were correct. This is certainly not the case in our software package (Oxford Instruments ISIS300), as quantification with Ge K or L yields different apparent concentrations, up to 10at% apart, as shown in figure 3a. Calculating the ratio

$$x_{\text{Ge}_K,L} / x_{\text{Si}_K} = (I_{\text{Ge}_K,L} k_{\text{Ge}_K,L} a_{\text{Ge}_K,L} / A_{\text{Ge}}) / (I_{\text{Si}} / A_{\text{Si}}) \quad (\text{eqn. 4})$$

for either K- or L-line of Ge and inserting $x_{\text{Si}_K} = 1 - x_{\text{Ge}}$ for the binary system, this can be solved for

$$k_{\text{Ge}_K,L}^* \equiv k_{\text{Ge}_K,L} a_{\text{Ge}_K,L} = (x_{\text{Ge}_K,L} I_{\text{Si}} A_{\text{Ge}}) / [(1 - x_{\text{Ge}}) I_{\text{Ge}_K,L} A_{\text{Si}}] \quad (\text{eqn. 5})$$

The product of k -factor and absorption factor (relative to Si) on the left side of equation 5 basically represents a thickness-dependent k -factor [10], which we have experimentally determined for two reference samples of known chemical composition, namely a bulk $\text{Si}_{0.54}\text{Ge}_{0.46}$ (the chemical composition of which has been confirmed independently as 46.8 ± 0.6 at.% Ge by inductively-coupled

plasma optical emission spectrometry using a Spectro Cirrus Vision instrument and a nitric acid/HF digest) and a strained layer $\text{Si}_{0.45}\text{Ge}_{0.55}$ sample (the Ge composition of the layered stack shown in figure 1 has been confirmed independently via strain analysis by X-ray diffraction, and the layer analysed here is the topmost in the stack with $x=0.552\pm0.002$). The X-ray spectra were acquired in a JEOL 2010F operated at 197kV and equipped with an Oxford Instruments Si:Li detector with ultrathin window. In the few cases where substantial Cu was detected from the supporting copper ring, a corresponding amount (in at.%) was subtracted from the Si signal to account for stray X-rays (some of which were present despite the use of an analytical stray aperture).

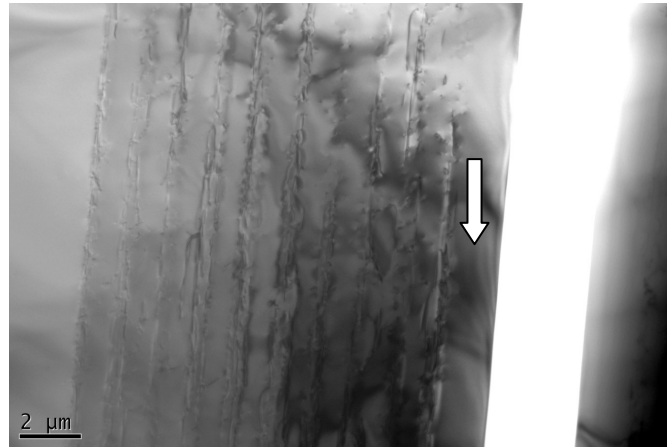


Figure 1. Bright field TEM image of a stack of 10 step-terraced grown SiGe buffer layers grown on Si(001) substrate (visible at the left). The $\text{Si}_{0.45}\text{Ge}_{0.55}$ layer investigated here was grown last and is marked by an arrow.

In figure 2 we plot for all spectra the $I_{\text{GeK}}/I_{\text{GeL}}$ ratio vs. detector dead time, which can be assumed to be proportional to the specimen thickness projected along the electron beam direction [15]. Data points lie on straight lines the slope of which depends on tilt angle, composition (higher Ge content means higher density and thus stronger absorption, i.e. higher slope) and also the beam intensity, however, the intercept with the vertical axis is the same. This gives an estimate of the Ge K/L intensity ratio of 1.3 for a specimen of zero thickness ($t=0$) which is difficult to achieve in practice. Note that some measurements for small thicknesses led to considerable carbon built-up on the sample surface, thereby absorbing preferentially the softer L-line (hence, larger apparent K/L ratios). These spectra are marked by open symbols and were omitted from fitting.

Figure 3 shows plots of the thickness dependent k -factors from equation (5) as a function of the Ge K/L ratio, i.e. of $k^*_{\text{GeK,L}}$, along with exponential and also parabolic fits, for both Ge K-line (a) and L-line (b) from the same set of spectra taken under various conditions. It can be seen that data from both samples fall onto common lines for both X-ray lines. The “correct” k -factors $k_{\text{GeK,L}}$ for ultra-thin samples would then be obtained from an extrapolation to zero thickness. Using the K/L line ratio extrapolated above and the second-order polynomial fits in figure 3, we calculate these k -factors for ideal thin samples as $k_{\text{GeK,Si}} = 1.53\pm0.08$ for the Ge K-line and $k_{\text{GeL,Si}} = 2.08\pm0.07$ for the Ge L-line. A comparison with the k -factors tabulated in the ISIS300 software in table 1 shows large differences, and in particular $k_{\text{GeL}} > k_{\text{GeK}}$, while the tabulated ISIS values would suggest the reverse.

If the ISIS software is used for quantification, without absorption correction the Ge L-line yields somewhat better results than the Ge K-line, however, the spread of the results is large (see figure 4a). While the true compositions lie somewhere between those values reported from K- or L-line quantification, simple interpolation will be inappropriate because the actual values determined at any point will vary with thickness and if a wider thickness range is included the average reported will systematically shift. Even if absorption is included (using an average density of $\rho=3.95\text{ g cm}^{-3}$ [16] and

assuming a linear interpolation between $t=0$ for Ge K/L=1.3 and $t=1200\text{nm}$ for K/L=2.5 [17]) the discrepancy between quantifications using either the Ge K- or the Ge L-line relative to Si K is only reduced but not eliminated, as demonstrated in table 1.

Relative uncertainties of 3-5% in our extrapolated k -factors should allow us to determine the Ge concentration to $\Delta x = \pm 0.02$ in thin specimens, where the precision is mainly limited by the spread of the K/L ratio determined from the extrapolation to $t=0$ in figure 2, i.e. ultimately the knowledge of the specimen thickness. Simply averaging over all spectra using these k -factors for ideal thin films without absorption correction then yields consistent values from both K- and L-lines, but the values are too large for higher sample thicknesses if no allowance is made for absorption (see figure 4c)

However, using K- or L-lines with the thickness dependent k^* -factors from figure 3 in which the mean squared deviation of all 55 data points from the fit curves is only $\langle(\Delta k^*)^2\rangle=0.014$ (figure 3a) to 0.039 (figure 3b) now implies mean relative errors in k^* for any spectrum of 1-3% and leads to nearly identical results for both samples *independent of thickness*, as demonstrated in figure 4d, with an rms spread of only $\sqrt{\langle\Delta x^2\rangle}=\pm 0.01$. The scatter observed is mainly due to counting statistics, and the deviation of the average of repeated measurements from the nominal values are typically $\Delta x < 0.005$.

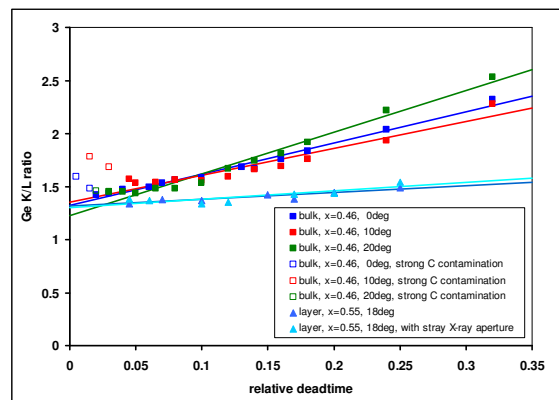


Figure 2. Plot of Ge K/L intensity ratio vs. detector dead time, for two calibration samples of $x_{\text{Ge}}=0.46$ and 0.55 studied at various tilts towards the X-ray detector, along with linear fits. Extrapolation to zero dead time (for an ideal thin sample) yields an intercept of 1.303 ± 0.047 for all five curves. The linear regression coefficients are $R^2=0.943 \pm 0.059$.

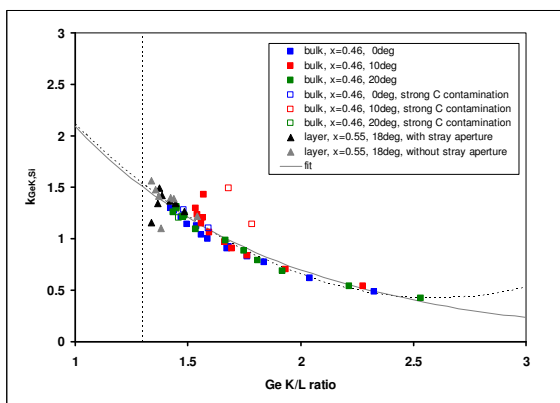


Figure 3a. Plot of the ratio $k^*_{\text{GeK}} = k_{\text{GeK}} a_{\text{GeK}}$ vs. Ge K/L intensity ratio for both samples. Solid [dotted] lines indicate exponential [parabolic] fits, respectively, which yield nearly identical values for an intensity ratio K/L=1.303 \pm 0.047 for $t=0$ of $k_{\text{GeK}}=1.501 \pm 0.077$ [1.529 \pm 0.081].

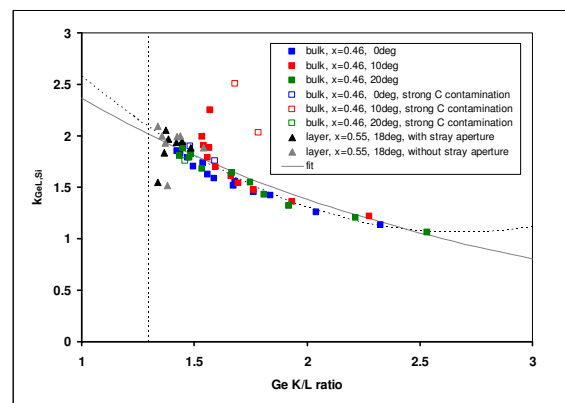


Figure 3b. Plot of the ratio $k^*_{\text{GeL}} = k_{\text{GeL}} a_{\text{GeL}}$ vs. Ge K/L intensity ratio for both samples. Solid [dotted] lines indicate exponential [parabolic] fits, respectively, which for $t=0$ extrapolate to $k_{\text{GeL}}=2.015 \pm 0.051$ [2.080 \pm 0.070].

Table 1. Comparison of k -factors (with respect to Si_K) and reported germanium concentrations

specimen		k -factor		bulk sample ($x_{\text{Ge}}=0.468$)		strained layer ($x_{\text{Ge}}=0.552$)	
method	line	Ge K	Ge L	Ge K	Ge L	Ge K	Ge L
ISIS, thin film approximation ($a=1$)		1.723	1.651	0.597±0.070	0.462±0.045	0.609±0.024	0.516±0.024
ISIS, with absorption correction for linear increase of thickness from $t=0$ (K/L=1.3) to $t=1200\text{nm}$ (K/L=2.5)		1.723	1.651	0.524±0.033	0.423±0.026	0.584±0.024	0.503±0.025
k^* -factor extrapolated to K/L=1.303 from parabolic fit, then used without absorption correction ($a=1$)		1.53±0.08	2.08±0.07	0.569±0.072	0.519±0.045	0.581±0.024	0.573±0.023
k^* -factor for K/L ratio as measured for each spectrum	figure 3a	figure 3b		0.464±0.012	0.461±0.011	0.545±0.010	0.548±0.012

Note: font colour indicates whether numerical results agree with reference within error bars (green) or not (red). When numerical results are correct but error bars >0.02, the error bars are marked yellow.

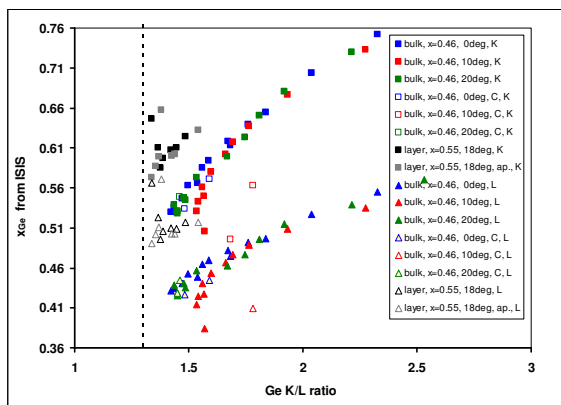


Figure 4a. Plot of x_{Ge} from LINK ISIS300 calculated without absorption correction. Numerical results differ for K and L lines and strongly vary with thickness.

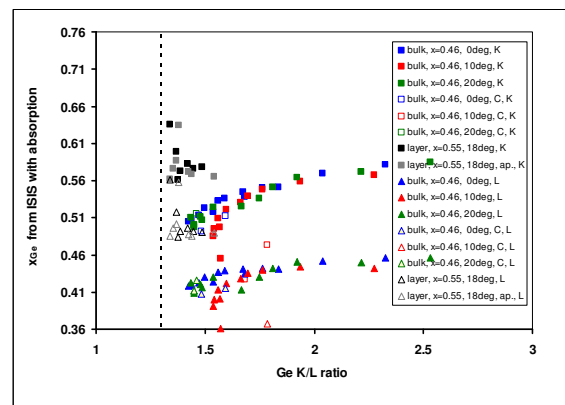


Figure 4b. Plot of x_{Ge} from LINK ISIS300 calculated with absorption correction. Numerical results still differ for K and L lines but vary somewhat less with thickness.

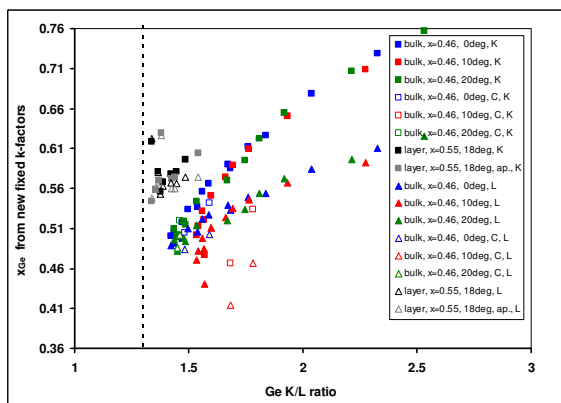


Figure 4c. Plot of x_{Ge} from k -factors extrapolated to $t=0$ as in [10]. Results from K and L lines now agree better but still depend on thickness, and are too large throughout.

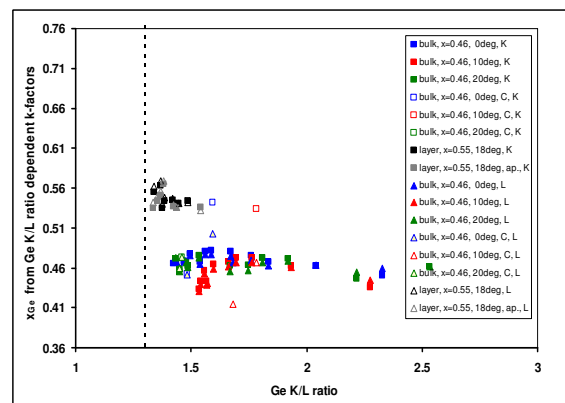


Figure 4d. Plot of output x_{Ge} using improved k^* -factors, i.e. $k^*_{\text{Ge},K,L}$ from figure 3. Results from K and L lines agree within noise levels and are independent of thickness.

3. Summary

By plotting the k -factor in EDXS versus the intensity ratio of two suitable lines (e.g. K/L) it is possible to define an effective k -factor (k^*) for each X-ray line which implicitly performs an absorption correction without knowledge of the absolute specimen thickness. For thicker and/or denser specimens and/or smaller take-off angles the absorption of K- and L-lines will be affected differently, and rather than computing this effect numerically for sets of specimen thicknesses, densities and take-off angles we can simply use the effective k -factors from calibration curves (such as in figure 2) at the appropriate K/L ratio to account for the different absorption effects. Applying this to two SiGe specimens of known compositions we have shown that we can determine the germanium concentration in a self-consistent way to better than 1at% for a specimen of unknown thickness, at least in the range of $t \leq 1.2 \mu\text{m}$ which should be sufficient for most experimental cases.

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