Accurate calibration for the quantification of the Al content in AlGaN epitaxial layers by energy-dispersive X-ray spectroscopy in a Transmission Electron Microscope

H Amari\textsuperscript{1}, L Lari\textsuperscript{1}, H Y Zhang\textsuperscript{1}, L Geelhaar\textsuperscript{2}, C Chèze\textsuperscript{2}, M J Kappers\textsuperscript{3}, C McAleese\textsuperscript{3}, C J Humphreys\textsuperscript{3} and T Walther\textsuperscript{1}

\textsuperscript{1} Department of Electronic & Electrical Engineering, University of Sheffield, Sir Frederick Mappin Building, Mappin Street, Sheffield S1 3JD, UK
\textsuperscript{2} Paul-Drude-Institut für Festkörperelektronik, 10117 Berlin, Germany
\textsuperscript{3} Department of Materials Science & Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK

E-mail: h.amari@sheffield.ac.uk

Abstract. Since the band structure of group III-nitrides presents a direct electronic transition with a band-gap energy covering the range from 3.4 eV for (GaN) to 6.2 eV (for AlN) at room temperature as well as a high thermal conductivity, aluminium gallium nitride (AlGaN) is a strong candidate for high-power and high-temperature electronic devices and short-wavelength (visible and ultraviolet) optoelectronic devices. We report here a study by energy-filtered transmission electron microscopy (EFTEM) and energy-dispersive X-ray spectroscopy (EDXS) of the microstructure and elemental distribution in different aluminium gallium nitride epitaxial layers grown by different research groups. A calibration procedure is outlined that yields the Al content from EDXS to within ~1 at % precision.

1. Introduction
A range of electron microscopy techniques can be used to monitor changes in elemental distributions, thicknesses of layers and the effects of different types of dislocations. Reliable elemental distribution mapping by EDXS in a (scanning) transmission electron microscope (TEM/STEM) depends upon knowledge of different parameters for each line, such as the absorption (A) \cite{1} and the fluorescence (F) \cite{2} coefficients. This approach also includes atomic number (Z) \cite{3} effects and has become known as ZAF correction. This correction to energy-dispersive X-ray microanalysis is important for accurate quantification, in particular for low atomic number materials. In order to calibrate EDXS for determining the chemical composition of AlGaN accurately within ~1 at%, this project compared experimental measurements of X-ray line intensity ratios obtained by EDXS from four different AlGaN layer samples that covered a wide compositional range from Ga-rich (Al\textsubscript{0.23}Ga\textsubscript{0.77}N) to Al-rich (Al\textsubscript{0.87}Ga\textsubscript{0.13}N). Particular attention is drawn to the effects on the intensities of the Al-K, Ga-K and Ga-L lines by stray X-rays from the Al\textsubscript{2}O\textsubscript{3} (corundum) substrate and by potential Ga implantation during focused Ga\textsuperscript{+}-ion beam thinning. Usually, the thickness of a specimen for TEM is not precisely known but can influence the ZAF correction significantly. Hence, unknown sample thicknesses are a major
source of error in quantitative EDXS. Here, we follow an approach where the X-ray signals are measured as function of known thicknesses to eliminate this source of errors [4].

2. Sample growth
AlGaN/GaN and AlGaN/AlN heterostructures were grown by different methods on α-alumina (corundum) substrates. To reduce the dislocation density in the Ga-rich sample (Al$_{0.23}$Ga$_{0.77}$N), a 140 nm GaN buffer layer was grown on top of (0001) Al$_2$O$_3$ at a temperature of 700°C by molecular beam epitaxy (MBE), followed by the Al$_{0.23}$Ga$_{0.77}$N layer at 800 °C [5]. For the other three samples with higher Al content a thick AlN buffer layer (~ 4 µm) was deposited on (0001) Al$_2$O$_3$ at a temperature of 1130 °C by metal-organic chemical vapour deposition (MOCVD), followed by 2 µm Al$_x$Ga$_{1-x}$N layers ($x = 0.44$, 0.72, and 0.87) at 1090 °C [6]. The Ga and Al concentrations were investigated by Rutherford Back Scattering (RBS) or X-ray diffraction (XRD).

3. TEM experiments
The focused ion beam (FIB) technique has been employed to prepare electron transparent specimens. This technique allowed us to mill site-specific windows into the lamella samples of known sample thicknesses in the range 50 – 700 nm. The TEM analysis was carried out in a JEOL 2010F field-emission gun TEM/STEM microscope operated at 197 keV and equipped with an energy dispersive X-ray spectrometer (Oxford Instruments Si:Li detector with ultra thin window and Link ISIS 300 acquisition software), annular dark field (ADF) (55 mrad inner angle) and bright field (BF) STEM detectors coupled with a Gatan Digiscan system, and a Gatan GIF 2000 Imaging Filter.

4. Results and Discussion

4.1. STEM and EFTEM analyses
The FIB milling was employed for sample preparation in order to obtain regions with different calibrated thicknesses ($t$) as shown in Fig. 1. The BF images in Fig. 1 show the lamella structures studied in this work. In Fig.1(a) the 134 nm GaN and the 139 nm AlGaN layers appear darker because of their higher mean atomic number with respect to corundum (substrate) on the bottom and the carbon region on the top. Fig. 2 shows columnar grain growth in both GaN buffer layer and AlGaN layer, which are separated by a rough interface.

![Figure 1](image_url)

**Figure 1.** BF images showing the lamella structures including AlGaN/GaN or AlN/Al$_2$O$_3$ for (a) Al$_{0.23}$Ga$_{0.77}$N, (b) Al$_{0.44}$Ga$_{0.56}$N, (c) Al$_{0.72}$Ga$_{0.28}$N, and (d) Al$_{0.87}$Ga$_{0.13}$N. Numbers indicate regions of different thicknesses.

The sample thickness ($t$) was obtained using Energy-Filtered Transmission Electron Microscopy (EFTEM). It was measured locally, as shown in Fig. 2(b), in units of the total mean free path, $\lambda$, for inelastic scattering, obtained via the EELS routines of Gatan Digital Micrograph.
Figure 2. (a) BF image showing Al$_{0.23}$Ga$_{0.77}$N/GaN/Al$_2$O$_3$ interfaces. (b) EFTEM thickness map of region 1 of the first structure (arrows indicate positions of thickness measurements and EDXS point analyses reported below). Grey levels: Black: $t/\lambda = 0$, White: $t/\lambda = 4.76$.

Table 1. Thicknesses measured from relative thickness maps using the inelastic mean free paths of the materials for a collection angle of $\beta = 40$ mrad employing Egerton’s approximation [7].

| sample                | 1  | 2  | 3  | 4  | 5  |
|-----------------------|----|----|----|----|----|
| Al$_{0.23}$Ga$_{0.77}$N | 86 | 160| 280| 427| 700|
| Al$_{0.44}$Ga$_{0.56}$N | 64 | 82 | 127| 214| 390|
| Al$_{0.72}$Ga$_{0.28}$N | 105| 142| 250| 416| 600|
| Al$_{0.87}$Ga$_{0.13}$N | 103| 184| 221| 316| 443|

4.2. Determination of local composition by EDXS

Operating at 197 keV, the minimal electron probe of the JEOL 2010F is around 0.25 nm diameter, but in order to investigate the Al distribution in individual thin layers by a series of EDX point analyses in STEM mode, a probe size of 1 nm was used which, along the beam direction through the sample, will broaden to several nm. All the EDX spectra were acquired for acquisition times of 300 s, an energy resolution of 120 eV, and an energy dispersion of 20 eV/channel. The concentration of element $j$ was obtained using the ISIS 300 X-ray quantification routine [8], based on the following formula:

$$x_j = \frac{I_j\times k_j\times a_j/A_j}{\sum_i [k_i\times k_i\times a_i/A_i]} \quad (1)$$

where $x$ is the elemental concentration in atomic percent (at%), $I$ the integral intensity of the peak of interest (background subtracted), and $k$, $a$, $A$ are $k$-factor (for weight %), absorption and the atomic weight respectively. Since EDX analysis for low atomic number elements such as N is not accurately enough, only Al-K, Ga-K and Ga-L peaks were considered. In Table 2, we list $k$-factors and absorption factors relative to Si-K as a standard which are used in our calculations. Fig. 3 presents typical EDX spectra of two different structures: Al$_{0.23}$Ga$_{0.77}$N/GaN/Al$_2$O$_3$ (left side), and Al$_{0.87}$Ga$_{0.13}$N/AlN/Al$_2$O$_3$. Even though the accuracy of EDX analysis for light elements is poor, a quantitative analysis of Al, Ga, N, and O has been attempted. It can be seen that the layers contain all these elements; Cu and C signals are due to the specimen support grid and surface contamination. In the EDX spectrum obtained from Al$_2$O$_3$, we attributed the weak Ga peak (~ 0.3 at %) to Ga implantation related to the FIB sample preparation method. Also, because the Al$_{0.23}$Ga$_{0.77}$N layers are thinner than the Al-richer AlGaN samples, the presence of the apparent Al peak in the GaN spectrum is due to beam broadening and the vicinity of the corundum substrate.
Table 2: list of $k$-factors and absorption factors relative to Si-K that ISIS uses for Al and Ga ratio calculations for different thicknesses with an effective take-off angle of 45° (25° + 20° tilt of specimen towards detectors). AlGaN densities are; 5.45 for Al$_{0.23}$Ga$_{0.77}$N, 4.8 for Al$_{0.44}$Ga$_{0.56}$N, 4.1 for Al$_{0.72}$Ga$_{0.28}$N, and 3.7 for Al$_{0.87}$Ga$_{0.13}$N.

| line | $k$-factor | abs. fact | abs. fact | abs. fact | abs. fact | abs. fact |
|------|------------|-----------|-----------|-----------|-----------|-----------|
| Al-K | 1.03       | 1.007     | 0.995     | 0.952     | 0.956     | 1.009     |
| Ga-K | 1.609      | 0.966     | 0.969     | 0.898     | 0.589     | 0.407     |
| Ga-L | 1.654      | 0.955     | 0.989     | 0.846     | 0.743     | 0.680     |

Figure 3. Typical EDX spectra acquired from Al$_2$O$_3$ substrate (below), GaN or AlN buffer layers (middle) and AlGaN epitaxial layers (above) respectively; (left side: Al$_{0.23}$Ga$_{0.77}$N/GaN at $t \approx 90$ nm, right side: Al$_{0.87}$Ga$_{0.13}$N/AlN at $t \approx 100$ nm).

The composition ratio of Al to Ga is close to the nominal stoichiometric values for all AlGaN layers except the narrowest Al$_{0.23}$Ga$_{0.77}$N and GaN layers, where the analyses points were much closer to the substrate. To estimate the combination of beam broadening and stray X-rays, EDX spectra were acquired in the GaN buffer layer, as shown in Fig. 4. The Al contribution from Al$_2$O$_3$ is fitted by a polynomial extrapolation of the curve in Fig. 4 to $t = 0$ nm. It was made sure by electron energy-loss spectroscopy (EELS) that the GaN layer did not actually have any noticeable Al contamination. The quadratic behaviour shown in Fig. 4 agrees with the electron beam broadening successively with larger specimen thicknesses, which yields more signal from the substrate region.
Assuming to a first approximation that the amount of Al-K stray X-rays from the substrate depends on the sample thickness as shown and linearly on the Ga-content of the layer investigated (as Ga is the heaviest element in our samples and mostly responsible for beam broadening and stray X-rays), we can calculate that a certain fraction \( \delta_{Al} \) of the intensity of the Al-K X-rays is due to stray scattering:

\[
\delta_{Al} = (bt^2 + ct + d) \times x_{Ga}
\]

where \( b, c \) and \( d \) are fitting constants, \( t \) is thickness and \( x_{Ga} = 1 - x_{Al} \) the nominal Ga content. Also, as mentioned above, Ga implantation by the FIB sample preparation method needs to be considered. The estimated contribution \( \delta_{Al} \) was obtained by the investigation of Ga in AlN buffer and Al\(_2\)O\(_3\) layers.

The results showed that a value of 0.3 at% should be subtracted from the Ga signal for improved calculations. To obtain corrected Al ratios \( \tilde{x}_{Al} \), the following equation was applied:

\[
\tilde{x}_{Al} = \frac{(I_{Al} - \delta_{Al}) \times k_{Al} \times a_{Al} / A_{Al}}{(I_{Al} - \delta_{Al}) \times k_{Al} \times a_{Al} / A_{Al} + (I_{Ga} - \delta_{Ga}) \times k_{Ga} \times a_{Ga} / A_{Ga}}
\]

Fig. 5 plots the results of the EDXS quantification for the different AlGaN layers obtained after the application of equation (3). As we can see we get a linear dependence of \( \tilde{x}_{Al} \) on thickness, which is weak for Al-rich AlGaN but strong for Ga-rich AlGaN.
Figure 6. Al fractions obtained by EDXS for thinnest (diamond symbols) and thickest (square symbols) regions for Al-K/Ga-K (solid symbols) and Al-K/Ga-L (open symbols) vs. concentrations from RBS/XRD (a) without any correction, (b) using equation (3), and (c) using equation (3) and extrapolation to $t=0$.

Table 3: Quantitative comparison of Al concentration from X-ray spectra of samples of different thicknesses after linear fitting of data.

| $x_{Al}$ without correction | thinnest regions | | thicker regions | | | Ga-line | slopes | y-offsets | Ga-line | slopes | y-offsets |
|-----------------------------|------------------|---|----------------|---|---|----------------|---|----------------|---|
| Ga-K                        | 0.962 ± 0.025    | 0.038 ± 0.017 | Ga-K | 0.962 ± 0.025 | 0.038 ± 0.017 |
| Ga-L                        | 0.930 ± 0.027    | 0.064 ± 0.018 | Ga-L | 0.930 ± 0.027 | 0.064 ± 0.018 |
| Ga-K                        | 0.868 ± 0.071    | 0.120 ± 0.046 | Ga-K | 0.868 ± 0.071 | 0.120 ± 0.046 |
| Ga-L                        | 0.831 ± 0.089    | 0.147 ± 0.057 | Ga-L | 0.831 ± 0.089 | 0.147 ± 0.057 |

| $\tilde{x}_{Al}$ with correction | thinnest regions | | thicker regions | | | Ga-line | slopes | y-offsets | Ga-line | slopes | y-offsets |
|---------------------|------------------|---|----------------|---|---|----------------|---|----------------|---|
| Ga-K                | 0.973 ± 0.025    | 0.027 ± 0.016 | Ga-K | 0.973 ± 0.025 | 0.027 ± 0.016 |
| Ga-L                | 0.939 ± 0.029    | 0.053 ± 0.019 | Ga-L | 0.939 ± 0.029 | 0.053 ± 0.019 |
| Ga-K                | 0.898 ± 0.077    | 0.089 ± 0.050 | Ga-K | 0.898 ± 0.077 | 0.089 ± 0.050 |
| Ga-L                | 0.870 ± 0.088    | 0.107 ± 0.057 | Ga-L | 0.870 ± 0.088 | 0.107 ± 0.057 |

| $\hat{x}_{Al}$ with correction | $t=0$ | | | | | Ga-line | slopes | y-offsets | Ga-line | slopes | y-offsets |
|-------------------------------|-------|---|---|---|---|----------------|---|----------------|---|
| Ga-K                          | 0.989 ± 0.019 | 0.013 ± 0.012 | Ga-L | 0.959 ± 0.017 | 0.037 ± 0.011 |
| Ga-L                          | 0.870 ± 0.088 | 0.107 ± 0.057 | Ga-K | 0.973 ± 0.025 | 0.027 ± 0.016 |

5. Conclusion

It has been demonstrated that the EDX analysis applying commercial software is not accurate enough to obtain quantification within ± 1 at%. This can be improved using our method of calibration, by:

1. analyzing samples under identical experimental conditions,
2. taking systematic experimental measurements of X-ray line intensity ratios of Al-K, Ga-K and Ga-L, as a function of known sample thickness,
3. subtracting the elemental contributions from substrate (for Al), and ion implantation (for Ga),
4. extrapolating all corrected Al concentration values to $t=0$ nm from a thickness series.

We determine the Al concentration with a precision of ~ ± 1 at %.

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