Nanoscale EELS analysis of elemental distribution and band-gap properties in AlGaN epitaxial layers

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Abstract. Aluminium gallium nitride (AlGaN) is a strong candidate for high-power and high-temperature electronic devices and short-wavelength (visible and ultraviolet) optoelectronic devices. For band-gap engineering of nitride layers, it is essential to be able to perform an accurate local measurement of their optical properties. In this work, core-loss electron energy loss spectroscopy (EELS), plasmon spectroscopy and valence EELS (VEELS) are compared for the investigation of the local chemistry and band-gap of AlGaN.

1. Introduction

EELS is often applied to characterize the optical and chemical properties of wide band-gap nitride compounds. While the core-loss region of an EEL spectrum provides information about the elemental distribution and the crystal structure of the material, the low-loss region contains information about the chemical composition and electronic structure as well as the optical properties of the specimen. In this work, core-loss EELS, plasmon and valence EELS (VEELS) are compared for the investigation of AlGaN layer samples that cover a wide compositional range from Ga-rich (Al0.23Ga0.77N) to Al-rich (Al0.87Ga0.13N).

2. Sample description

Different nitride heterostructures were used in our experiments. In the Ga-rich sample (Al0.23Ga0.77N), a 140 nm GaN buffer layer was grown at 700 °C on top of (0001) Al2O3 by molecular beam epitaxy (MBE) followed by the Al0.23Ga0.77N at 800 °C [1]. For the Al-rich samples a thick AlN buffer layer (~4 µm) was deposited on (0001) Al2O3 substrate by metal-organic chemical vapour deposition (MOCVD) followed by 2 µm AlxGa1-xN layers (x = 0.44, 0.72, and 0.87) deposited at 1090 °C [2]. The Al and Ga ratios were investigated by Rutherford Back Scattering (RBS) or X-ray diffraction (XRD).

3. Experimental

TEM specimens were prepared by focused ion beam (FIB) thinning which has been used to obtain sample thicknesses in the range 50 – 700 nm. Analytical electron microscopy was carried out in a JEOL 2010F field-emission TEM/STEM microscope operated at 197 keV and equipped with annular dark field (ADF) and bright field (BF) detectors coupled with a Gatan Digiscan system. For electron energy loss spectroscopy (EELS) a Gatan imaging filter (GIF 2000) was used.
4. Results and discussion

4.1. STEM and EFTEM analyses

Fig. 1 shows BF images of the Ga-rich and one of the three Al-rich structures studied in this work. The FIB milling was employed for obtaining window regions of different thicknesses \( t \) as shown. In the Ga-rich sample, the 134 nm GaN and the 139 nm AlGaN layer appear dark because of their higher mean atomic number with respect to sapphire (substrate), and both show columnar grain growth. We also note the formation of an oxide on top of the AlGaN epilayer in the Ga-rich sample. Using energy-filtered transmission electron microscopy (EFTEM), the sample thickness \( t \) was measured locally in different positions along the whole structure, as shown in Table 1, from relative thickness maps using the inelastic mean free paths \( \lambda \) of the materials for a collection angle of \( \beta = 40 \) mrad, via the EELS routines of Gatan Digital Micrograph, employing Egerton’s approximations for effective atomic number and mean energy loss [3]. Points presented along the growth direction in figure 1 indicate positions of thickness measurements obtained by EFTEM and reported in Table 1.

![Figure 1](image)

**Figure 1.** BF image of (a) Al\(_{0.23}\)Ga\(_{0.77}\)N/GaN/sapphire, and (b) Al\(_{0.44}\)Ga\(_{0.56}\)N/AlN/sapphire. Points indicate positions of thickness measurements by EFTEM reported in Table 1.

**Table 1:** Thicknesses measured by EFTEM.

| sample          | \( \lambda \) (nm) | \( t \) (nm) |
|-----------------|---------------------|-------------|
| Al\(_{0.23}\)Ga\(_{0.77}\)N | 90                  | 86          |
| Al\(_{0.44}\)Ga\(_{0.56}\)N | 93                  | 64          |
| Al\(_{0.72}\)Ga\(_{0.28}\)N | 99                  | 105         |
| Al\(_{0.87}\)Ga\(_{0.13}\)N | 103                 | 103         |

4.2. Determination of local composition by EELS

To investigate the Al and Ga distribution in AlGaN layers, a series of EELS analyses in TEM mode were applied. All core-loss EEL spectra were acquired with an energy resolution of 0.9 eV (measured from full width at half maximum (FWHM) of the zero loss peak (ZLP)), exposure times of 1s, dispersion of 1eV/channel, in diffraction mode with a convergence and collection semi-angle of about 0.8 mrad and 12.5 mrad, respectively. Typical core loss spectra including Al-K and Ga-L edges of GaN, Al\(_{1-x}\)Ga\(_x\)N, and AlN layers are presented in figure 2. The atomic ratio of Al to Ga \( \frac{x_{\text{Al}}}{x_{\text{Ga}}} \) was calculated using the cross-sections, \( \sigma \), from either Hartree-Slater or hydrogenic (plus white line) models in the Digital Micrograph quantification routine, based on the following formula:

\[
\frac{x_{\text{Al}}}{x_{\text{Ga}}} = \frac{\sigma_{\text{Al}}(\Delta, \beta)}{\sigma_{\text{Ga}}(\Delta, \beta)} \times \frac{I_{\text{Al}}(\Delta, \beta)}{I_{\text{Ga}}(\Delta, \beta)}
\]

where \( \sigma(\Delta, \beta) \) are the cross-sections under the corresponding ionization edges for integration window size \( \Delta \) and semi-collection angle \( \beta \), \( I_{i}(\Delta, \beta) \) are the intensities \( i = \text{Al, Ga} \).
To investigate the influence of the integration window on the quantification, we quantified our layers using different integration windows covering the range 50-250 eV, using the same settings for the offset and the width of the background for each element (see Table 2). Because we didn’t apply any de-convolution (the thickness of the samples varied from about \( t/\lambda \sim 0.6 \) to \( t/\lambda \sim 1 \)), it was essential to calculate all Al/Ga ratios by using the same integration window for both edges [4]. As we can see from Fig. 3 (a) which presents results from the Hartree-Slater model, the apparent Al composition ratio from EELS \( (x_{Al}/[x_{Ga}+x_{Al}]; \text{with } x_{Al}+x_{Ga} = 1) \) depends strongly on the integration window size for lower Al-content while it appears stable at higher Al-content.

**Table 2:** Energy window settings used for elemental quantifications of the core-loss spectra.

| element | background fit | integration window |
|---------|----------------|---------------------|
| Al      | -120           | 98                  |
| Ga      | -169           | 115                 |
| N       | -48            | 35                  |

**Figure 2.** Core-loss spectra of GaN (left), Al\(_{0.44}\)Ga\(_{0.56}\)N (middle) and AlN (right).

**Figure 3.** (a) Al and Ga ratio quantification using Hartree-Slater and (b) Al and N ratio using hydrogenic plus white line models, as a function of the width of the energy windows used for integrating the intensity after background subtraction. The latter quantification using the N K-edge produces apparent values > 1.
For the N edge, using a larger window for fitting the background gave inferior fits that crossed the spectrum at high energies, which we attribute to weak intensity oscillations in the loss region 300-350 eV due to carbon.

4.3. Determination of plasmon excitations

Low-loss spectra were collected using an energy dispersion of nominally 0.05eV/channel, assumed to be correct within a few %, and a typical acquisition time of 0.5s in order to limit the electron beam damage to the sample and also to limit energy drift. Fig. 4 depicts typical low-loss spectra from all the AlGaN samples showing two main characteristics: the main plasmon excitations at slightly different energies ($E_p$) and a peak superimposed at ~ 23 eV on the high-energy tail of the plasmon excitations for Ga-rich samples which is related probably to the transition from Ga 3d [5]. The experimental results shown in Fig. 4 demonstrate that within the compositional range of interest, $E_p$ is sensitively depending on both features.

![Figure 4. Comparison of experimental low-loss spectra of AlGaN.](image)

**Table 3:** plasmon peak energies.

| sample   | $E_p$ (eV) |
|----------|------------|
| GaN      | 19.15      |
| Al$_{0.23}$Ga$_{0.77}$N | 19.3      |
| Al$_{0.44}$Ga$_{0.56}$N | 20.25      |
| Al$_{0.72}$Ga$_{0.28}$N | 20.35      |
| Al$_{0.85}$Ga$_{0.13}$N | 20.55      |
| AlN      | 21         |

Plotting plasmon excitation as a function of $x_{Al}$ and performing a linear fit yields a 1.8eV shift with $x_{Al}$:

$E_p$ (eV) = (19.12 ± 0.16) + x (1.80 ± 0.25); with a linear correlation coefficient ($R^2$) = 0.9245.
4.4. Determination of band-gap

In addition to giving us information on plasmon excitations, the low-loss region of the spectra provides us with transitions across the band-gap. The main problems in looking at the band-gap directly are to separate the signal onset from the tail of the zero-loss peak and to take into consideration possible Cerenkov radiation. For the first problem, we believe that using a sufficiently high energy resolution (about 0.8 eV) and using the microscope with suitable experimental conditions (high energy dispersion of about 0.05 eV/channel and an acquisition time of 0.5 s) separating the onset of the band-gap from the zero loss background is possible. For the second problem, because of the small angular range of Cerenkov radiations (for the collection of significant Cerenkov contribution a small collection aperture of the order of ~0.1 mrad is needed) [6], we believe that using a collection angle of about 12 mrad will limit the influence of these radiations, which for AlGaN with a refractive index of \( n = 2.15 \) (AlN)…2.3 (GaN) could occur for acceleration voltages above 60 kV, but have actually not been observed by us. Also, nitrides cover a band-gap energy from 3.4 eV (for GaN) to 6.2 eV (for AlN), and above ~3 eV no radiative effects have been reported to influence the spectrum for thick samples [7].

To reveal directly the onset of the band-gap, we refer to one of the optical principles of direct transitions in semiconductors, according to which the intensity \( I \) has a square-root dependence on the band gap \( E_g \) [8], so accordingly, \( I \) would have a linear dependence on \( E_g \). Thus, by plotting \( I^2 \) vs. energy loss \( E \), as shown in Fig. 5, and extrapolating the linear region to zero, the value of the direct band-gap transition energy is obtained. We performed linear fits to the experimental spectra over energy ranges that started just above the maximum band-gap of AlN \( (E_g = 6.20 \text{ eV}) \) [9] and varied the upper range of the fitting interval until we obtained the best linearity (i.e. 6.25 to 13, 14, 15 eV etc…) (see Table 4).

![Figure 5](image-url) Comparison of the square of the intensity versus energy of (a) GaN, (b) Al\(_{0.23}\)Ga\(_{0.77}\)N, (c) Al\(_{0.44}\)Ga\(_{0.56}\)N, (d) Al\(_{0.72}\)Ga\(_{0.28}\)N, (e) Al\(_{0.87}\)Ga\(_{0.13}\)N, and (f) AlN.

As we can see from Table 4, there is a strong dependence of the band-gap on Al-content, which is in excellent agreement with theory. The best linearity was obtained almost for the same intervals (6.25 to ~14 eV) for most alloy compositions. Also, we note that the linear regression coefficient \( R^2 \) gives a direct measure of the uncertainty in the extrapolated band-gap, \( \Delta E_g \), which varied from ±0.1 eV (if \( R^2 > 0.99 \)) to ±0.3 eV (if \( R^2 \approx 0.93 \)) (see Fig 6).
Table 4: Band-gap measurements of all AlGaN layers.

| sample       | fit interval | $R^2$  | band-gap (eV) |
|--------------|--------------|--------|---------------|
| GaN          | [6.25-12]    | 0.9820 | 3.26 ± 0.15   |
| Al$_{0.24}$Ga$_{0.76}$N | [6.25-13.5] | 0.9709 | 3.67 ± 0.19   |
| Al$_{0.44}$Ga$_{0.56}$N | [6.25-14]   | 0.9335 | 4.79 ± 0.32   |
| Al$_{0.72}$Ga$_{0.28}$N | [6.25-14]   | 0.9744 | 5.05 ± 0.20   |
| Al$_{0.87}$Ga$_{0.13}$N | [6.25-15]   | 0.9934 | 6.09 ± 0.10   |
| AlN          | [6.25-15]    | 0.9917 | 6.40 ± 0.11   |

Linear fit: $E_g$ (eV) = (3.14 ± 0.20) + x (3.18 ± 0.31); with a linear correlation coefficient ($R^2$) = 0.9618.

Figure 6. Uncertainty of extrapolated band-gap vs. fitting quality expressed by $R^2$.

5. Conclusion
It can be concluded that EELS, at least under the experimental conditions described in this paper, gives direct access to the optical properties of AlGaN layers. Calculations of the band-gap using plots of the square of the intensity vs. energy-loss have shown good agreement with theory. Reproducible systematic changes have been observed in the plasmon excitations and the band-gap from Al$_x$Ga$_{1-x}$N as a function of the Al-content. H. Amari acknowledges funding by EPSRC under grant EP/F02374X/1.

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Corrigendum: Nanoscale EELS analysis of elemental distribution and band-gap properties in AlGaN epitaxial layers

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In our original paper graph (c) in Fig. 5 was missing some data. Figure 5 should be replaced by:

![Graphs comparing square of intensity versus energy for different AlGaN compositions](image)

Fig. 5 Comparison of the square of the intensity versus energy of (a) GaN, (b) Al₀.₂₃Ga₀.₇₇N, (c) Al₀.₄₄Ga₀.₅₆N, (d) Al₀.₇₂Ga₀.₂₈N, (e) Al₀.₈₇Ga₀.₁₃N, and (f) AlN.