Characterization of thickness, elemental distribution and band-gap properties in AlGaN/GaN quantum wells by aberration-corrected TEM/STEM

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Abstract. This work presents an investigation of the thickness, the chemical composition and the band-gap properties of AlGaN/GaN quantum wells grown by Metal-Organic Chemical Vapour Deposition (MOCVD) on sapphire (0001) substrates. Various methods of analysis by transmission electron microscopy (TEM) were used for the characterization of these layers, such as scanning transmission electron microscopy STEM, energy-dispersive X-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS). Annular dark-field STEM provides more accurate layer thicknesses and Al concentrations than EDXS profiling.

1. Introduction
Annular dark-field STEM (ADF-STEM) and X-ray point analysis and line scans were used to investigate the elemental distribution of AlGaN/GaN quantum wells with atomic resolution using a new spherical aberration-corrected TEM/STEM microscope equipped with both probe and imaging correctors and a cold field-emission gun operating at 300 kV (JEOL-R005). Also, plasmon loss spectroscopy and valence EELS (VEELS) were used to investigate the band-gap properties of thin AlGaN and GaN layers, and to compare them to measurements.

2. Sample description and experimental setup
GaN quantum wells (QW) with nominal thicknesses decreasing from 8 nm to 0.5 nm were embedded between 10 nm AlGaN barriers. The AlGaN/GaN layers were grown on the top of c-plane sapphire substrates. First, an AlGaN buffer layer was grown at 1210 °C, followed by the active region consisting of a multiple quantum well (MQW) structure with 5 GaN layers separated by 10 nm Al₀.₁₅Ga₀.₈₅N barrier layers grown at 1125 °C. Cross-sectional TEM samples were prepared by mechanical polishing and Ar⁺ ion milling using both Gatan precision ion polishing system (PIPS) at 5 kV, and Ar⁺ polishing at 3 kV in a Technoorg Linda IV3 system. TEM analysis was carried out in a JEOL R005 which can achieve a sub-50 pm electron probe with 28 mrad semi-angle and is equipped with an energy dispersive X-ray spectrometer (JEOL 50 mm² Si:Li detector with ultra thin window and related acquisition software), annular dark field (ADF) and bright field (BF) STEM detectors coupled with a Gatan Digiscan system, and a Gatan Imaging Filter model 865 GIF Tridium.
3. Results and Discussion

3.1. STEM analyses

The annular-dark field (ADF) image in Fig. 1a shows the structure investigated. The thick layer preceding the active region represents the AlGaN buffer. The active region with darker and brighter bands, perpendicular to the growth direction, as shown enlarged in Fig. 1b, represents the AlGaN barrier layers and GaN QWs respectively. The GaN QWs appear brighter because of their higher mean atomic number compared to the AlGaN layers.

The possibility to obtain images using large illumination angles in aberration corrected microscopy [1] allows us to visualize the Ga concentration in QWs with high spatial resolution as shown in Fig. 1b. Also, an intensity line profile across the active region was extracted from Fig. 1b and is shown in Fig. 1c.

The intensity profile and high resolution ADF-STEM images (Figs. 1d, 1e, 1f, 1g, and 1h) show the existence of all 5 GaN QWs and the decrease of the thickness of the layers from 8 to 0.5 nm. The 5th QW may be damaged by ion beam milling as it is located topmost and appears at lower contrast.

Fig. 1i shows a high resolution STEM image of the centre of a GaN QW taken near the [1-100] zone-axis. The lattice planes labelled $d_1$ (~2.6 Å) and $d_2$ (~1.6 Å) correspond to the basal (0001) and a-plane (11-20) distances, respectively.

Fig. 1 ADF images showing (a) overview of the structure, (b) 5 GaN QWs separated by AlGaN barrier layers, (c) ADF STEM intensity profile of the 5 GaN QWs, high magnification image of (d) 1st QW, (e) 2nd QW, (f) 3rd QW, (g) 4th QW, (h) 5th QW, and (i) high resolution STEM image of GaN lattice. A-G indicate positions of EDXS and EELS point analyses reported below.
The higher Ga concentration of the GaN QWs relative to the AlGaN barrier layers is reflected in the intensity profile in Fig. 1c. The Al content in AlGaN can be directly measured from the ADF intensity ratio (R) of the centre of the GaN QW relative to the AlGaN [2], as presented in Table 1(a).

| QW # | t (nm) | R      |
|------|--------|--------|
| 1    | 8.03   | 1.170 ± 0.040 |
| 2    | 3.94   | 1.174 ± 0.047 |
| 3    | 2.09   | 1.150 ± 0.053 |
| 4    | 1.05   | 1.111 ± 0.058 |
| 5    | 0.54   | 1.062 ± 0.064 |

Table 1 (a) Comparison of peak GaN/AlGaN intensity ratios, (b) evaluation of Al concentrations for \( \varepsilon = 1.6 \) and \( \varepsilon = 2 \).

Assuming the quantum wells were all pure GaN, the Al content in Al\(_x\)Ga\(_{1-x}\)N can be obtained using the following approach [2]:

\[
\frac{I_{\text{Ga}N}}{I_{\text{AlGaN}}} = R = \frac{Z_{\varepsilon}^x + Z_{\varepsilon}^N}{xZ_{\varepsilon}^x + (1-x)Z_{\varepsilon}^A + Z_{\varepsilon}^N}
\]

where \( R \) is the ratio obtained from the intensity profile, \( x \) the elemental Al concentration in atomic percent (at %), \( Z \) the atomic number, and \( \varepsilon \) lies somewhere between 1.6 and 2 [2]. Table 2(b) lists the Al concentrations obtained from equation (1) for \( \varepsilon = 1.6 \) and \( \varepsilon = 2 \). For the two widest QWs the assumption is probably valid, which suggests \( x_{Al} \approx 0.19 \) in the AlGaN, and \( x_{Al} \approx 0.10 \) in the thinnest QW, demonstrating interdiffusion.

3.2. EDXS analyses

Using a probe size of less than 1 nm along the beam direction, EDX spectra were acquired at points A, B, C, D, E, F, and G as shown in Fig. 1b, for acquisition times of 30 s, and an energy resolution of \( \pm 130 \) eV. Figs. 2a and 2b depict typical EDX spectra acquired at points A and B in Fig. 1b.

![Fig. 2](a) Typical EDX spectra acquired from (a) AlGaN barrier layer, (b) GaN QW, and (c) EDX line scan across the GaN QWs.

The concentration of Al was obtained using the JEOL X-ray quantification routine, considering only Al-K, Ga-K and Ga-L peaks. The sample thickness \( t \) was estimated using low-loss energy spectra acquired close to the positions A, B, C, D, E, F and G in Fig. 1b using a convergence angle of \( 21 \) mrad and a collection angle of \( 1.75 \) mrad. The corresponding thickness was obtained via the compute thickness rule using the EELS routines of Gatan Digital Micrograph [3]. The quantitative comparison of Al concentrations from X-ray spectra of different thicknesses are shown in Table 2. The presence of a weak Al peak in the GaN spectrum (points B, D, and F) is due to beam broadening so that probe tails extend from the thin GaN QW into the AlGaN barrier layers. This can also affect calculations of Al:Ga ratios in AlGaN barriers. As the layers are very thin EDX point analyses were performed slightly off the zone-axis but with the layers edge-on, resulting in
fewer counts. To estimate the beam broadening effect \( b \) for a thickness \( t \sim 40\) nm, we used the following equation [4]:

\[
b = 7.21 \times 10^5 x \left( \frac{Z E_0}{\rho A} \right)^{0.5} t^{1.5}
\]

where \( Z \) is the atomic number, \( E_0 \) the beam energy in keV, \( \rho \) the density in g cm\(^{-3}\), and \( A \) the atomic weight [4]. The beam broadening is estimated as \( \sim 1.35\) nm. In addition, an X-ray line scan has been carried out, as shown in Fig. 2c. Since Al substitutes Ga atoms in III-V nitrides, the Al content in the AlGaN and GaN layers can be calculated from the corresponding depletion of the Ga-K signal, which is \( \sim 14\) at% for the 1\(^{st}\) QW.

3.3. EELS analyses

Low-loss EEL spectra were acquired in STEM mode with an energy resolution of 0.5 eV (measured from full width at half maximum (FWHM) of the zero loss peak (ZLP)), exposure times of 1s, and dispersion of 0.05 eV/channel. Typical low-loss spectra from AlGaN and GaN layers are presented in Fig. 3 which shows, first, the main plasmon excitations are positioned at different energies \( E_p = 19.36\) eV for AlGaN and \( E_p = 19.28\) for GaN, and second, the strong Ga M\(_{4,5}\) edge in the GaN spectrum positioned at \( \sim 23\) eV compared to the AlGaN spectrum.

![Fig. 3 Square of experimental low-loss intensity from the GaN QW (blue) and the Al\(_{0.15}\)Ga\(_{0.85}\)N barrier layer (grey).](image)

For direct transitions in semiconductors, the intensity \( I \) has a square-root dependence on the band gap \( (E_g) \). If we plot \( I \) vs. energy-loss \( (E) \) and extrapolate the linear fitting of the experimental spectra over energy range from 6.25 to 14 eV to zero, we can determine the bandgap as the crossing of the abscissa [5]. We obtain \( E_g = 3.80 \pm 0.50\) eV with a linear regression coefficient \( (R^2) \) of \( \sim 78\% \) for Al\(_{0.15}\)Ga\(_{0.85}\)N, and \( E_g = 3.16 \pm 0.50\) eV with the \( R^2 \) of \( \sim 77\% \) for GaN, which is in good agreement with previous work [6], and suggests \( x_{Al} \approx 20\% \) in the AlGaN barrier, in agreement with the above ADF data.

4. Conclusion

Thicknesses, elemental distribution and band-gap properties were obtained for AlGaN/GaN quantum wells using different analytical techniques in an aberration corrected electron microscope. Thickness measurements of the multilayers were found in agreement with the nominal values. The Al concentrations of AlGaN extracted from Z-contrast imaging were found to be larger and the values from EDX to be lower than the nominal Al concentration of 15\%. It can also be concluded that VEELS shows changes in the plasmon excitations and band-gap properties from different layers.

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