A systematic comparison of polar and semipolar Si-doped AlGaN alloys with high AlN content

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Abstract

With a view to supporting the development of ultra-violet light-emitting diodes and related devices, the compositional, emission and morphology properties of Si-doped n-type Al_{x}Ga_{1-x}N alloys are extensively compared. This study has been designed to determine how the different Al_{x}Ga_{1-x}N crystal orientations (polar (0001) and semipolar (11–22)) affect group-III composition and Si incorporation. Wavelength dispersive x-ray (WDX) spectroscopy was used to determine the AlN mole fraction (x ≈ 0.57–0.85) and dopant concentration (3 × 10^{18} – 1 × 10^{19} cm^{-3}) in various series of Al_{x}Ga_{1-x}N layers grown on (0001) and (11–22) AlN/sapphire templates by metalorganic chemical vapor deposition. The polar samples exhibit hexagonal surface features with Ga-rich boundaries confirmed by WDX mapping. Surface morphology was examined by atomic force microscopy for samples grown with different disilane flow rates and the semipolar samples were shown to have smoother surfaces than their polar counterparts, with an approximate 15% reduction in roughness. Optical characterization using cathodoluminescence (CL) spectroscopy allowed analysis of near-band edge emission in the range 4.0–5.4 eV as well as various deep impurity transition peaks in the range 2.7–4.8 eV. The combination of spatially-resolved characterization techniques, including CL and WDX, has provided detailed information on how the crystal growth direction affects the alloy and dopant concentrations.

Keywords: AlGaN, crystal orientation, alloy composition, III-nitride semiconductors, Si doping, cathodoluminescence, x-ray microanalysis

(Some figures may appear in colour only in the online journal)
1. Introduction

Al$_{x}$Ga$_{1-x}$N is a promising material for optoelectronic devices such as ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes operating in the wavelength range from 210 to 365 nm, depending on the AlN mole fraction $x$ [1–3]. It is also possible to control Al$_{x}$Ga$_{1-x}$N properties such as spontaneous and piezoelectric polarization constants, and lattice constants through group-III compositions in order to obtain the optimal characteristics for the target nitride devices [4]. Most Al$_{x}$Ga$_{1-x}$N layers are grown on sapphire substrates due to limited availability of native AlN substrates (generally only with small diameters, typically about 1”, and at very high cost). Heteroepitaxy on sapphire substrates usually results in growth of Al$_{x}$Ga$_{1-x}$N layers with high threading dislocation densities due to the lattice and thermal expansion coefficient mismatches [5, 6]. These are significant challenges for the production of high quality AlN-rich Al$_{x}$Ga$_{1-x}$N films needed for devices [2]. Al$_{x}$Ga$_{1-x}$N-based LEDs have attracted a lot of attention, with a view to increasing the low emission efficiencies for devices emitting below 300 nm [3]. This lower emission efficiency is a result of various factors, including high dislocation densities, high resistivity and poor light extraction efficiency [7]. Al$_{x}$Ga$_{1-x}$N-based deep-ultraviolet (DUV) LED bare dies with external quantum efficiencies (EQEs) of 3.5% at 265 nm, over 4.5% at 270 nm, and over 6% between 280 nm and 300 nm without encapsulation and with a p-GaN contact layer have been reported [7, 8]. However, for LEDs emitting around 250 nm, EQEs remain around 2% [1]. One of the major requirements for the device fabrication is successful doping with Si, which is the most common donor for $n$-type Al$_{x}$Ga$_{1-x}$N layers [9, 10]. The Si doping changes the structural, electrical and optical properties of the Al$_{x}$Ga$_{1-x}$N material. The main changes are in electric conductivity [11], but there are also changes in luminescence efficiency [12], optical polarization [13], point defect-density [13, 14], and mechanical strain [15], particularly through the phenomenon of dislocation inclination [16]. As the AlN fraction increases above 0.8 it becomes increasingly challenging to obtain high conductivity [10, 17]. This effect arises from the self-compensation effects of the Si donor and from a transition of Si from a shallow donor to a DX center [18, 19]. In turn this leads to an increase in activation energy $E_A$ of Si with increasing AlN fraction [10, 17]. Other factors that influence carrier compensation in the Al$_{x}$Ga$_{1-x}$N material are threading dislocations, unintentional impurities and native defects [20].

Trap states introduced by defects in the bandgap often reduce the electrical conductivity [21]. They can be associated with specific luminescence peaks from AlGaN, making it possible to use the cathodoluminescence (CL) spectroscopy employed in this work to confirm the existence of different defects. A range of defects are present in AlGaN, including cation vacancies (V$_{\text{III}}$)$_{\text{V}}$ and defect complexes comprising the cavity vacancy plus oxygen, with either one or two negative charges. These defects have small formation energies in AlN-rich AlGaN and are easily formed in undoped and Si-doped AlGaN layers [22]. Mehnke et al. [23] showed how the drop in the resistivity of AlGaN: Si layers is related to the self-compensation effects that may be attributed to the increasing formation of vacancies or vacancy-oxygen complexes with increasing Al content. It has been confirmed that the increase of the resistivity with increasing Al is mainly caused by a decrease in the carrier density [23, 24]. For the set of samples studied, compensation effects were confirmed for semipolar and polar samples, where for the optimized (A4SP) sample a carrier concentration of $\sim 1.2 \times 10^{19}$ cm$^{-3}$ was measured but on further increase in the Si/III ratio (sample A5SP) the carrier concentration and mobility decreased, indicating the beginning of Si over-compensation [25]. For the polar set of samples, a significant amount of the conductivity was due to phonon-assisted hopping among localized states in the impurity band. Free-carrier concentration in the conduction band has already reached its maximum of $1.6 \times 10^{18}$ cm$^{-3}$ at a Si/III ratio of $2.8 \times 10^{-5}$ cm$^{-3}$ (sample A1P) and any further increase of dopant atoms supplied during growth only enhances the impurity-band conduction with concentrations of the carriers participating in this type of transport that increase from $2.1 \times 10^{18}$ cm$^{-3}$ up to $4.3 \times 10^{18}$ cm$^{-3}$. This process eventually stops when a critical Si/III ratio is reached and the band-like channel starts to degrade (i.e. at sample A4P) and above [26].

Using CL to identify the suppression of these vacancy complex defects will lead to further improvements in the conductivity.

In the case of the semipolar AlGaN a minimum resistivity of 0.018 $\Omega$cm was reported for the optimised layer with 60% AlN content (A4SP) [25]. For semipolar AlGaN samples with 60% AlN content Jo et al. reported resistivity of 0.009 $\Omega$cm [27]. For the polar samples with 60% AlN content the reported resistivity values were much higher, e.g. $\sim 10 \Omega$cm for sample A1P [26]. The resistivity in high AlN content AlGaN has been shown to increase steeply from 0.026 $\Omega$cm to 2.62 $\Omega$cm as AlN content increased from 82%–95% [23].

Traditionally, Al$_{x}$Ga$_{1-x}$N is grown in the polar (0001) c-plane orientation because it is relatively easy to obtain higher material quality in this orientation. The drawback of this orientation is that the corresponding structures suffer from a strong polarization-induced quantum confined Stark effect and exciton localization [28, 29]. Growth in semipolar directions can significantly reduce the polarization-induced electrical fields. Furthermore, exciton localization in semipolar Al$_{x}$Ga$_{1-x}$N is significantly reduced compared to c-plane Al$_{x}$Ga$_{1-x}$N due to a reduction in alloy compositional fluctuations [30, 31]. As a consequence, semipolar Al$_{x}$Ga$_{1-x}$N has significant potential in terms of improving the performance of DUV LEDs.

This paper reports on a systematic study of polar and semipolar $n$-type doped Al$_{x}$Ga$_{1-x}$N:Si/AlN layers grown on sapphire by metalorganic chemical vapor deposition (MOCVD) with varied Si/group-III ratios in the gas phase. High AlN alloy fraction samples were investigated because the difference in the lattice constants between the Al$_{x}$Ga$_{1-x}$N and the AlN layer decreases with increasing AlN alloy fraction, reducing the density of misfit dislocations [32]. Systematic reports comparing the optical properties of semipolar and polar Al$_{x}$Ga$_{1-x}$N...
Wavelength dispersive x-ray (WDX) microanalysis and CL spectroscopy were used to evaluate the doping characteristics and optical properties of a wide range of Si-doped Al\(_x\)Ga\(_{1-x}\)N layers (n-Al\(_x\)Ga\(_{1-x}\)N). The samples studied were 0.8–1.1 µm-thick layers with Si concentrations ([Si]) in the range from \(2 \times 10^{18}\) cm\(^{-3}\) to \(1 \times 10^{19}\) cm\(^{-3}\), grown along polar (0001) and semipolar (11–22) planes.

2. Experimental

The Al\(_x\)Ga\(_{1-x}\)N films were grown in an Aixtron 3 × 2 inch close-coupled showerhead MOCVD reactor on (0001)- and (11–22)-oriented AlN/sapphire templates for polar and semipolar samples, respectively. The templates were prepared as described in [33] and [34] for polar and semipolar orientations, respectively. Trimethylgallium (TMGa) and trimethylaluminium (TMAI) were used as group-III precursors, and ammonia (NH\(_3\)) was used as the nitrogen precursor. H\(_2\) was used as the carrier gas and disilane (Si\(_2\)H\(_6\)) as the doping source. The AlN fraction was controlled by varying TMAI/(TMGa + TMAI) ratio, V/III ratios and growth rate. Three series of experiments were performed at different growth conditions, varying the Si\(_2\)H\(_6\)/III ratio while keeping all other parameters nominally fixed. In the first series, polar (A1P to A5P) and semipolar (A1SP to A5SP) samples were grown simultaneously with the reactor pressure of 50 mbar, and growth temperature of 1100 °C. In the second series, only polarsamples (B1P to B5P) were grown at 50 mbar and 1115 °C. Finally, polar (C1P to C5P) and semipolar (C1SP to C5SP) samples were grown simultaneously at 200 mbar and 1100 °C. For each group of the samples V/III ratio and TMAI/(TMGa + TMAI) ratio are listed in table 1. These quite significantly different conditions resulted in variations between the series in terms of average compositions and growth rates; the latter were found to be about 0.23, 0.66 and 0.31 nm s\(^{-1}\) for series A, B and C, respectively. The thickness of the doped films in all experiments was kept within the range of 800–1100 nm. More details on the growth of polar samples in series A and B are also given in [28] and for semipolar samples in the series A in [29]. The AlN alloy fraction and the dopant concentration were determined using WDX measurements. Note that the AlN fractions quoted in [29] were measured by x-ray diffraction, which results in slight differences. Before the WDX examination,

| Label | Crystal orientation | \(\frac{\text{TMAI}}{\text{TMGa} + \text{TMAI}}\) ratio | Approx. growth rate (nm \(^s\)) | Si\(_2\)H\(_6\)/III ratio \((\times 10^{-7})\) | V/III ratio | WDX Si content \((10^{18} \text{ cm}^{-3})\) | AlN fraction x |
|-------|---------------------|-----------------|-------------------------------|-------------------|-------------|------------------------|---------------|
| A1P   | (0001)              | 0.5             | 279                           | 4                 | 0.69        | 0.63                   |
| A2P   |                     |                 | 558                           | 4                 | 0.72        |                        |
| A3P   |                     | 0.23            | 1120                          | 600               | 5           | 0.69                   |
| A4P   |                     |                 | 2230                          | 8                 | 0.63        |                        |
| A5P   |                     |                 | 3350                          | 10                | 0.70        |                        |
| A1SP  | (11–22)             | 0.5             | 1120                          | 600               | 7           | 0.61                   |
| A2SP  |                     |                 | 2230                          | 8                 | 0.60        |                        |
| A3SP  |                     | 0.66            | 328                           | 460               | 10          | 0.85                   |
| A4SP  |                     |                 | 437                           | 4                 | 0.75        | 0.82                   |
| A5SP  |                     |                 | 656                           | 5                 | 0.84        |                        |
| B1P   | (0001)              | 0.824           | 328                           | 460               | 10          | 0.85                   |
| B2P   |                     |                 | 437                           | 4                 | 0.85        |                        |
| B3P   |                     |                 | 656                           | 5                 | 0.84        |                        |
| C1P   | (0001)              | 0.333           | 449                           | 23                | 4           | 0.82                   |
| C2P   |                     |                 | 561                           | 4                 | 0.82        |                        |
| C3P   |                     | 0.31            | 749                           | 6                 | 0.82        |                        |
| C4P   |                     |                 | 112                           | 3                 | 0.81        |                        |
| C5P   |                     |                 | 299                           | 5                 | 0.82        |                        |
| C1SP  | (11–22)             | 0.333           | 449                           | 23                | 3           | 0.77                   |
| C2SP  |                     |                 | 561                           | 7                 | 0.75        |                        |
| C3SP  |                     | 0.31            | 749                           | 3                 | 0.76        |                        |

Materials should be valuable with a view to guiding improvements in material quality.

Table 1. Sample series details.
all samples and composition standards (AlN, GaN and Si) were carbon-coated to reduce the effect of charging. WDX measurements were performed with an electron probe microanalyzer (EPMA, JEOL JXA-8530F) at an acceleration voltage of 10 kV and a beam current of 40 nA. At these conditions, the interaction volume is kept within the first 800 nm of the Al\(_x\)Ga\(_{1-x}\)N layers according to Monte Carlo simulations using CASINO software [35]. For WDX point measurements quantitative data is an average of nine independent measurements selected away from larger 3D features across the sample surface. Any longer range compositional variations in the bulk film were below the detection limit of the WDX measurements. In the quantitative analysis x-ray line intensities emitted from the main specimens (\(L_\alpha\) for Ga and \(K_\alpha\) for Al, N, Si) were compared against the same x-ray line from the standard samples with known concentrations (AlN, GaN and Si). The measured intensities were then corrected for differences in composition between the standard and main specimens using an iterative procedure to give accurate atomic percentages of the species [36]. For estimating the Si concentration, a calibration method was used. The method involves measuring the Si intensity of all samples and comparing with Al\(_x\)Ga\(_{1-x}\)N and GaN reference samples for which Si concentration was known from secondary ion mass spectrometry (SIMS) analysis [37, 38]. Dopant densities evaluated by this method are in the range of \(10^{17} - 10^{19}\) cm\(^{-3}\). The concentration determined directly from the WDX are over-estimated, likely as a result of surface contamination [38].

The surface quality was examined using secondary electron (SE) imaging in a low-vacuum field emission gun scanning electron microscope (FEG-SEM, FEI Quanta 250 FEG). The morphology was also investigated using a Veeco multimode V atomic force microscope (AFM) in tapping mode. Images were also acquired in backscattered electron (BSE) mode, yielding compositional contrast dependent on the average atomic number of the material (Z).

CL spectra were recorded from uncoated samples in the low-vacuum FEG-SEM with a chamber pressure of 1 mbar, electron beam voltage of 15 kV and a beam current of 14 nA. Spectra were recorded with a spectral resolution of 0.8 nm, using a spectrometer with a 600 lines/mm grating blazed at 200 nm, a 50 \(\mu\)m slit, a focal length of 125 mm, and a 1600-element charge-coupled device. CL maps were recorded with the same spectrometer at 0.5 mbar chamber pressure [39]. The optical information obtained using CL was combined with the SE imaging to provide highly spatially resolved correlation of topography and optical properties [12].

3. Results and discussion

3.1. Surface morphology of the n-Al\(_x\)Ga\(_{1-x}\)N films

The surface morphology was examined by AFM for samples grown with different Si\(_2\)H\(_6\) flow rates (1 and 3 sccm). The root mean square (RMS) roughness values were examined for 2 \(\mu m \times 2 \mu m\) scan areas, giving average values of 4.35 and 3.76 nm for the polar and semipolar samples, respectively. The semipolar samples were found to have smoother surfaces than their polar counterparts, with an approximate 15% reduction in RMS. The surfaces of the semipolar samples are stable and not changed with different Si\(_2\)H\(_6\) flow rates [40, 41].

Figure 1 shows BSE micrographs of representative n-Al\(_x\)Ga\(_{1-x}\)N films grown on AlN/sapphire. The surface of polar sample C4P reveals brighter regions around hexagon edges (figure 1(c)), which is indication of a locally lower AlN alloy fraction [12]. These are less clear in the lower AlN alloy fraction polar layer (A1P) shown in figure 1(a), but become apparent using the WDX mapping, which is discussed later. The surfaces of semipolar samples A4SP and C4SP reveal considerably fewer three-dimensional (3D) features (figures 1(b) and (d), respectively).

In general, due to the lattice mismatch between Al\(_x\)Ga\(_{1-x}\)N and the underlying AlN layer, the resulting compressive strain can be relaxed either through formation of additional dislocations (favored for Al\(_x\)Ga\(_{1-x}\)N with high x) or through enhanced surface roughening (preferable for low x) [42]. However in the case of n-Al\(_x\)Ga\(_{1-x}\)N with high doping levels (\(>10^{18}\) cm\(^{-3}\)) and typical crystal quality (total dislocation density \(\sim 10^6\)) - \(10^{10}\) cm\(^{-2}\)), tensile strain gradually builds-up during the Al\(_x\)Ga\(_{1-x}\)N growth [43].

All the c-plane samples show hexagonal platelet structures and small hillock grains; additionally differently oriented crystallites are observed on their surfaces with no visible pits. The suppression of 3D nucleation for higher AlN alloy fraction c-plane samples is expected, due to the lower diffusion length of Ga adatoms at the higher TMAI flux necessary for their growth [44]. Also, compressive stress is reduced with increasing AlN alloy fraction in Al\(_x\)Ga\(_{1-x}\)N/AlN and thus reduced defect formation is expected [42]. However, neither of the above effects are observed in our samples, as shown later in figures 5(c), (d) and (e).

There is no clear correlation between the diameter of the hexagonal platelets and the Si\(_2\)H\(_6\) flow rate. The average hexagon diameter varies between 3.5 and 7 \(\mu m\). Some similar samples have been assumed to be free from stress due to the occurrence of 3D growth [45] but in the present case the layers are smooth on a macroscopic scale and still under stress, as shown by x-ray diffraction measurements (not shown here). The polar layer deposited at a high V/III ratio of 600 (figure 1(c)) shows a rough surface morphology with some pyramidal hillocks of different sizes. On the other hand, the layer deposited at a lower V/III ratio of 23 (figure 1(c)) shows a similar morphology, but with similarly sized hexagons on the surface. For the c-plane samples in the B series, the surface morphology seems to be optimal with the intermediate V/III ratio of 460 (figure 1(e)). For the polar samples in the series C, there is a trend of increasing diameter of hexagonal platelets with increasing Si concentration. It may be possible that Si doping favors the stabilization and development of crystallographic facets [46]. There is no obvious correlation between Si concentration and the smoothness of surface morphology due to the enhanced mobility of the adatoms.

The set of semipolar samples (A and C) appears to have formed a continuous film, as seen in figures 1(b) and (d). For the same V/III ratio, their AlN fraction is lower compared to...
Figure 1. BSE micrographs of the Al$_x$Ga$_{1-x}$N layers with polar (left column) and semipolar (right column) orientations, details in table 1.

3.2. WDX measurement

Table 1 presents the WDX measured compositions and doping levels for all the samples. Each of the reported values is the mean of nine measurements, chosen arbitrarily across the sample surface. The standard errors calculated for the AlN atomic fractions are 0.02–0.05, likely caused by compositional inhomogeneities on the samples, as they are too large to be purely caused by the technique limitations. The overall weight total for each of the samples investigated (the sum of mass percentages for all independently measured elements) was (100 ± 2) %, confirming a successful WDX analysis for the major elements.

Comparing the measured AlN alloy fraction for the samples within the same series but of different crystal orientations,
one can see that AlN alloy fraction is lower in the semipolar samples, in agreement with [40], although there are reports of different relationships between AlN alloy fraction and orientation [41, 47]. For the samples with high V/III ratios, the AlN alloy fraction values are also lower due to increased TMAl:NH$_3$ pre-reactions and the suppression of GaN decomposition at increased ammonia fluxes [26, 48]. For example, for the semipolar samples in series A, grown with a V/III ratio of 600 and TMAl/(TMGa + TMAl) ratio of 0.5, the AlN alloy fraction is estimated to be 0.57–0.65 as compared with the samples in the series C, grown with the lower V/III ratio of 23 and TMAl/(TMGa + TMAl) ratio of 0.333, where it is estimated to be 0.75–0.78 (table 1).

Figure 2 shows the measured Si concentration of the n-Al$_x$Ga$_{1-x}$N layers as a function of Si$_2$H$_6$ to group-III ratio. There is a general trend of linearly increasing Si concentration with increasing Si/III ratio, although with a significant scattering of data. At a Si/III ratio above 2.3 $\times$ 10$^{-4}$ a saturation of the Si concentration is observed for the semipolar samples in series A (ASP). The semipolar samples in series C (CSP) have lower Si/III ratios and although it is harder to be definitively about saturation, it is noted that the Si concentration drops for the highest Si/III ratio.

The saturation point is consistent with the work from Dinh et al [25], who used Hall data to show that the carrier concentration and mobility of the semipolar ASP layers reach a maximum at a similar Si/III ratio. The polar samples in series A (AP) exhibit an almost linear increase of [Si] with increasing Si$_2$H$_6$ flow rate, with no evidence of saturation. Interestingly, the trend is very different from the co-loaded semipolar samples (series ASP) with a much higher Si incorporation for A2SP (compared to A2P) followed by a saturation for A4SP. The polar samples in series B (BP) lie on a line parallel to the samples in series A, with the exception of B3P, which has a much higher Si incorporation. Hall-effect measurements for the polar samples in series B show a monotonic decrease of the Hall coefficient with increasing Si$_2$H$_6$ flow rate [26], strongly indicating that sample B3P is anomalous. For the polar samples in series C (CP), [Si] seems to lie roughly on the same line as the A and B sets. The polar C series shows an approximate linear increase with Si/III ratio. However, the Si/III ratios do not extend above 0.75 $\times$ 10$^{-4}$ in both C series and the [Si] measurements for the semipolar CSP samples show significant scatter.

3.3. WDX mapping

According to Mogilatenko et al [42], the difference in AlN fraction of the Al$_x$Ga$_{1-x}$N regions on planar c-plane terraces and on the side facets of the surface macrosteps corresponds to at least 0.1 (10% AlN fraction) for $x = 0.6$ and around 0.04 (4% AlN fraction) for $x = 0.8$.

Due to difference in surface mobility between Al and Ga adatoms the lowest Ga incorporation happens on the top facets of the hexagons [45], while Al adatoms are readily incorporated onto any Al$_x$Ga$_{1-x}$N surface due to their lower surface diffusion length [49]. Ga adatoms have a longer diffusion length increasing the chance of incorporating at an energetically more favorable site or being irreversibly desorbed to the ambient. From our observations, it is clear that with hexagonal features in sample C1P, Ga will be trapped around the feature edges, resulting in an increased Ga incorporation. However, on the feature top surfaces, effective areas are larger and smoother, leading to a faster Ga diffusion. That is one of the reasons why a GaN-rich phase is noticeable at the boundaries of 3D surface features [45, 50]. A possible explanation for this observation is that island boundaries provide additional chemical bonds where Ga can be retained, resulting in Ga accumulation [50].

The experimental data for the polar sample C1P in figure 3 show a higher (lower) intensity of Ga L$_x$ (Al K$_x$) x-rays around the hexagon edges; the same behavior is observed in the compositional BSE image. Comparing these maps allows us to rule out topographic effects as the dominant source of contrast, in which an increased backscatter signal would result in fewer x-ray counts. Seeing bright edges in both therefore unambiguously points to higher mass regions in a way that either map alone would not. Despite the challenging signal-to-noise ratio, inherent to x-ray counting statistics, we can see clear variations in the Ga distribution on a sub-μm length scale. The GaN alloy fraction was quantified using the measured GaN at% from WDX quantitative point data giving an estimate of 18% GaN at the middle of the map (figure 3(b)). The observed difference from center to edge of a hexagon is about 2% GaN. In contrast, a WDX map of a semipolar sample (A5SP), whose surface is free from hexagons, does not reveal any observable variation between Ga L$_x$ and Al K$_x$ x-rays (therefore not presented), indicating better compositional homogeneity compared to polar samples.

3.4. CL mapping

CL hyperspectral mapping enables us to correlate optical properties with surface morphology by mapping variations in
s spectral luminescence across a sample [51, 52]. The acquired CL images can be simultaneously or sequentially (as in this work) correlated with WDX spot analyses or maps, thus enabling specific CL characteristics to be related to semiconductor composition [52].

CL spectra were measured for all samples, and maps collected for selected polar samples. The spectra revealed near-band edge (NBE) peaks in the photon energy range of 4.0–5.4 eV and impurity transition peaks in the range of 2.7–4.8 eV. An example of a typical CL spectrum is shown in (figure 4(b)), for the sample C1P.

The impurity transitions are assigned to recombination between shallow donors and deep level acceptors including cation vacancies (V$_{\text{III}}$) and V$_{\text{III}}$ complexes (e.g. (V$_{\text{III}}$–O)$_2$) [53].

One of the explanations for the introduction of the vacancy type defects is related to the transition of the growth mode from 2D growth to 3D growth [14]. Cation vacancies act as nonradiative recombination centers in Al$_x$Ga$_{1-x}$N, and it is possible that they are introduced by Si doping due to a decrease in their formation energy as the Fermi level moves towards the conduction band [20].

The CL intensity maps (figures 4(c)–(f)), extracted from the hyperspectral data set, reveal domains between which there are shifts in the Al$_x$Ga$_{1-x}$N NBE emission energy. The 2D CL intensity maps were extracted from the 3D data cube by integrating over a given spectral window, while calculating a centroid over the same range generates a map of emission energy [54].

Regions of higher CL intensity in the NBE peak intensity map (figure 4(c)) correlate with lower emission energy in the corresponding NBE intensity map (figure 4(d)), following the same trend as compositional variations revealed by the WDX mapping (figure 3(b)). While these alloy variations are likely the dominant cause of the observed peak shift, additional contributions from non-uniform elastic strain and carrier concentrations cannot be discounted.

Figure 4(c) reveals an increase in the NBE intensity all the way along the edges of the hexagons compared to the middle of the feature. The intensity map of the (V$_{\text{III}}$ complex)$^{–}$ defect peak, figure 4(e), seems to be more localized and higher intensity spots are observable along the edges of the hexagon. Oxygen can possibly be more easily incorporated at the semi-polar facets of the hexagons [12].

For the other two defect peaks ((V$_{\text{III}}$ complex)$^{–}$ and (V$_{\text{cation}}$)$^{–}$) a higher intensity is measured from the middle of hexagon, figure 4(f), which contrasts with the behavior of the other peaks. A screw dislocation has been reported to emerge at the middle of the hexagon [12], with which the defect complex (V$_{\text{cation}}$)$^{–}$ could be related, additionally we found that the AlN composition is higher in the middle of the hexagons which could lead to a locally lower formation energy of these defects.

At the edges of the hexagon, the growth conditions differ from the rest of the sample, as discussed above. In the case of the c-plane sample C1P (81% AlN), the hexagon center shows 98% of the mean whole map intensity and the edge 101%.

For sample A1P (63% AlN), the difference in NBE intensity from different parts of the sample is larger (the center of hexagon shows 95% of the mean map intensity and the edge 109%). Also, the shift in the NBE emission energy from center to edge is found to be larger in this case of 110 meV compared to 60 meV for C1P (figure 4(d)). The CL map of sample A1P not presented as it demonstrates exactly the same type of luminescence behavior as seen in sample C1P. This shift for sample C1P corresponds to a difference of about 1.5% in GaN content, which compares well with the 2 at% GaN difference estimated from the WDX map. From these observations, it is apparent that the sample grown with the highest V/III ratio of 600 and with $x < 0.63$ (A1P) shows higher compositional inhomogeneity compared to the sample grown at lower V/III ratio of 23 and with $x > 0.81$ (C1P).

3.5. CL spectra

Figure 5 shows mean CL spectra for all c-plane and semi-polar sample series. It is noticeable that the intensities of the deep impurity transitions are on the same order or higher than those of the band-edge transitions. Each set of CL spectra (figures 5(a)–(e)) represents samples with a particular V/III ratio and orientation, and shows how the relative intensity of the NBE peaks and impurity transitions, depend strongly

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Figure 3. Composition mapping of the c-plane sample C1P (81% AlN mole fraction). (a) BSE image of the measured area, (b) GaN content map (at%) obtained from a WDX map of the Ga $L_\alpha$ x-ray intensity.
Figure 4. CL imaging of the c-plane C1P sample: including SE image (a), mean CL spectrum (b) and $5 \times 5 \mu m^2$ CL maps of the sample (c)-(f).

on the growth conditions. Similar behavior was reported in [12, 25]. Figure 6 plots the peak wavelengths of the impurity transitions observed in the spectra as a function of AlN content, alongside previously published data [29], in order to clarify the origins of the peaks.

The spectra in figures 5(a), (b) and (e) (which correspond to the polar and semipolar samples in the series A, and polar samples in the series C, respectively) reveal ($V_{III}^{1}$), ($V_{III}^{2}$), ($V_{III}^{3}$) impurity peaks and NBE peaks. For the polar samples in the series A, the intensity of the NBE peak increases with Si content, as well as the intensity of the ($V_{III}^{1}$) peak for A1P–A4P samples. ($V_{III}^{1}$) peak decreases again for A5P where the ($V_{III}^{2}$) becomes strongest. The ($V_{III}^{2}$) peak becomes visible in higher Si content samples (A3P–A5P) and follows the same trend, with the intensity of the peak
Figure 5. Room temperature (300 K) CL spectra of $n$-Al$_x$Ga$_{1-x}$N layers: (a) $c$-plane layers (series A), $x = 0.63–0.72$, (b) semipolar layers (series A), $x = 0.57–0.65$, (c) $c$-plane layers (series B), $x = 0.84–0.85$, (d) semipolar layers (series C), $x = 0.75–0.78$, (e) $c$-plane layers (series C), $x = 0.81–0.82$.

Increasing with Si content. The $(V_{III})^{3−}$ intensity is highest for lowest Si content samples (A1P and A2P). As described earlier, WDX and Hall data indicate that the Si incorporation saturated in the semipolar ASP series and it is notable that the $(V_{III} \text{complex})^{1−}$ and $(V_{III} \text{complex})^{2−}$ peaks are hardly present in the CL spectra from the more highly doped samples in this series. This may be related to a low solubility limit for Si in the semipolar samples, although further research is needed to confirm this.

For the polar samples in series C, the intensity of the NBE decreases with increasing [Si], as well as the intensity of the $(V_{III} \text{complex})^{2−}$ peak as seen in figure 5(e).

For the polar samples in the series B and the semipolar samples in the series C the $(V_{III} \text{complex})^{1−}$ is not
Figure 6. CL peak positions of deep impurity transitions obtained from figure 5 as a function of AlN-alloy fraction. The results from this work (black and white symbols) are plotted against previously published data (colored symbols) from [29] for comparison. The solid lines provide guides to the eye.

present, as shown in figures 5(c) and (d). The V_{III} complex with oxygen is only visible in figure 5(d) for the semipolar samples in the series C. Oxygen can behave as an electron acceptor in Al$_x$Ga$_{1-x}$N and hinder $n$-type behavior achieved with Si doping, similar to cation vacancies [19, 20, 55]. The aforementioned complex could be associated also with N vacancies, since the growth was performed at very low V/III ratio of 23 [48].

4. Conclusion

The compositional and optical properties of semipolar (11–22) and polar (0001) $n$-Al$_x$Ga$_{1-x}$N films have been systematically investigated using WDX and CL measurements. The Si-doping concentration was measured by WDX, using calibration data from SIMS.

Comparison of the measured AlN alloy fraction for samples with different crystal orientations showed that the AlN incorporation was higher in the polar samples. The highest values of Si incorporations were observed for the polar samples with the highest Si/III ratios, while saturation of Si incorporation was seen for the semipolar samples at higher Si/III ratios.

CL hyperspectral imaging of the polar samples revealed significant reductions in NBE luminescence intensity from the middle of surface hexagonal features where a threading dislocation is expected to be terminated. WDX mapping confirmed higher Ga incorporation around the hexagon edges. The semipolar samples showed no such features, corresponding to a better compositional homogeneity. CL point spectra showed how changes in the relative intensity of the NBE peaks and impurity transitions depend strongly on the growth conditions and surface orientations.

The main implication of this work for LED research is the use of the CL technique to identify the suppression of impurity defects, which will lead to further improvements in the layer conductivity since they act as recombination centers. The analysis of CL data can therefore help reduce point defect densities by guiding the optimization of growth parameters. The technique is potentially also informative for other layers grown under similar conditions where point defects cannot be directly measured, such as quantum wells. The CL and WDX results presented in this paper provide information on how point defect incorporation in the doped AlGaN contact layers is influenced by crystal orientation, alloy composition, and Si incorporation, as well as on the existence of different compensating defects. This paper also highlights challenges associated with growth of high AlN content AlGaN layers such as occurrence of hexagonal platelet structures in c-plane samples and compositional inhomogeneity.

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Data availability

The datasets that support the findings of this study can be found online under DOI: 10.15129/a7c54205-9bca-4785-9b3e-16e2a1b182771.

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