Composite GaN-C-Ga (‘GaCN’) Layers with Tuneable Refractive Index

Sourish Banerjee, Arnoud J. Onnink, Satadal Dutta, Antonius A. I. Aarnink, Dirk J. Gravesteijn and Alexey Y. Kovalgin*

MESA+ Institute for Nanotechnology, University of Twente, P.O Box 217, 7500AE Enschede, The Netherlands

**Figure S1.** The combined N 1s – Ga L$_2$M$_{45}$M$_{45}$ Auger peaks spectrum of the reference GaN sample.
Supporting Information

**Figure S2.** The Ga 2p3/2 spectrum of the reference GaN sample.

**Figure S3.** The XRD θ-2θ spectrum of a GaCN sample compared with a grazing incidence (GIXRD) spectrum of the reference GaN sample.
**Figure S4.** The different d-spacing values obtained in the polycrystalline (regions 1, 2) and amorphous (region 3) regions of the interstitial matrix (see Figure 4 for matrix definition) of GaCN. These graphs are obtained by radial profile analysis of the power spectrum (Fourier transform) of HRTEM micrographs.

**Figure S5.** EDX analysis performed at the three different features (as observed in Figure 4b) of the GaCN layer: column, inclusion and matrix. The Cu peak is due to the instrument.
Figure S6. (a) Zero-energy-loss TEM image of the GaCN region where the Energy Filtered TEM (EFTEM) analysis was performed. (b-d) Elemental maps showing the spatial inhomogeneity of Ga, C and N in the layer, computed with 3-window elemental mapping on the electron energy loss spectrum (EELS) of Ga, C and N elements.
Supporting Information

Figure S6. (e) Elemental maps of Ga, C and N (shown separately as Ga & C and C & N) from two slices in the GaCN layer, showing a spatial distribution of the elements (Ga in blue, C in red, N in green). The dimension of the slices is 57 nm x 12 nm, the specimen thickness is estimated to be 41 nm. The spatial variation of the elemental intensities inside the slices is shown above the elemental maps. Based on the correlation between the intensities, regions I and II in slice 1, and region III in slice 2 have been identified to contain different chemical species. Summary of the analysis can be found in Table 1.

Table S1. Assignment of various regions in the GaCN layer, based on the EFTEM elemental maps of Figure S6e. Symbols ↑, ↓ and “-” denote an increase, a decrease and no significant change in the elemental intensity, respectively. The region-assignment has been done based on a simultaneous change of the respective elements’ intensity. For example, in region I there is a finite but relatively unchanging N intensity, whereas the Ga and C intensities show increase and decrease, respectively. The near-unchanged N intensity is associated with the N-containing material present above or below the region, and likely not associated with it. Accordingly, region I is assigned as a Ga cluster.

| Region | Size (nm) | Intensity | Assignment |
|--------|-----------|-----------|------------|
| I      | 17        | ↑ ↓ -     | Ga cluster |
| II     | 10        | - ↑ ↑     | C=N cluster |
| III    | 14        | ↑ - ↑     | GaN cluster |
**Supporting Information**

**Figure S7a.** Dependence of the refractive index \( (n) \) (at 1500 nm) on the C-content in GaCN.

**Figure S7b.** Dependence of the extinction coefficient \( (k) \) at different wavelengths (600, 800, 1000, 1200 and 1400 nm) on the C-content in GaCN layers. Both graphs: the statistical error is within the symbol size, not exceeding 0.001 (see next section for details).

**Figure S8.** Dependence of the optical bandgap \( (E_g) \) on the C-content from GaN to GaCN layers.

**Figure S9.** Ratio of the 286.3-to-283.5 eV band-area plotted versus the C-content. The bands are assigned to C=N and C-Ga bonds in the C 1s XPS spectrum, respectively.
Spectroscopic ellipsometry (SE) data analysis. The ellipsometric parameters $\Psi$ and $\Delta$ describe the change in the polarization of light that is reflected from the sample. The complete theory is described elsewhere\textsuperscript{1}. To summarize, $\Psi$ and $\Delta$ are related to the reflection coefficients for p- and s-polarized light, $R_p$ and $R_s$, by $\frac{R_p}{R_s} = \tan \Psi e^{i\Delta}$. By modelling the sample as a stack of $j$ layers (Figure S10), $R_p/R_s$ can be calculated as a function of the layer thicknesses $D_1, D_2, \ldots, D_j$, the angle of incidence $\theta$ and the optical functions $n_1(\lambda), n_2(\lambda), \ldots, n_j(\lambda)$ and $k_1(\lambda), k_2(\lambda), \ldots, k_j(\lambda)$, where $n$ denotes the refractive index, $k$ the absorption coefficient and $\lambda$ the wavelength. Non-linear regression by the Levenberg-Marquardt algorithm\textsuperscript{2} finds the best fit of these parameters to the experimental data. The statistical error in the parameters is determined from the curvature matrix of the Marquardt method\textsuperscript{2} and confirmed for all points ($n$ and $k$) in figure S7 by bootstrap analysis\textsuperscript{5} included in J.A. Woollam CompleteEASE 5.19 software.

To account for the roughness of the surface, the top layer is described as a mixture of voids (volume fraction 0.5) and the deposited material (fraction 0.5, optical constants linked to the bulk layer) by the Bruggeman effective medium approximation (EMA)\textsuperscript{1,3,4}.

| Rough surface of composite layer (5-15 nm) |
|------------------------------------------|
| Thickness is fitted                      |
| Optical function is a Bruggeman effective medium approximation\textsuperscript{1,3,4} (EMA) combining the optical functions of void (fraction 0.5) and the underlying layer (fraction 0.5). |

| Composite layer GaN/Ga/C (70-130 nm) |
|--------------------------------------|
| Thickness is fitted, for each location on wafer individually |
| Optical function is fitted with a single model for all locations on wafer (Parameterizations: B-spline\textsuperscript{6}, Cody-Lorentz\textsuperscript{7}, and Sellmeier\textsuperscript{1,8}) |

| AlN (25 nm) |
|-------------|
| Thickness from in-situ SE during growth |
| Optical function determined from ex-situ VASE + reflectance on an AlN-only reference sample (MSA) |

| Si substrate |
|--------------|
| Optical functions from literature\textsuperscript{9}. |

Figure S10. Multi-layer model for the fitting of SE and reflectance data. The use of VASE and MSA to obtain unique solutions for thickness and refractive index is explained in the text.

Figure S11 compares experimental data at the center point on wafer# 74141 (10% of carbon) to fits using three different parameterizations for $n(\lambda)$ and $k(\lambda)$ of the composite layer.

- Cubic B-spline parameterization can describe any dielectric function that is consistent with the Kramers-Kronig relations\textsuperscript{1,6} (within the limits of the node spacing; here 0.3 eV) and can thus reveal any effect that inclusions (such as gallium or carbon) may have on the optical functions. Therefore, the results in the main text are obtained by B-spline parameterization. The corresponding reduced $\chi^2$ value ($r\chi^2$) for a multi-sample analysis (MSA) of the entire dataset (16 VASE and reflectance spectra) is 7.321.
- Oscillator functions such as Cody-Lorentz\textsuperscript{7} assume a specific form for the optical constants based on a physical model. The Cody-Lorentz parameterization includes the Urbach tail discussed in the main text, and describes the experimental SE data for all samples with comparable $r\chi^2$ (7.986 for the 10% carbon sample) and optical constants (Figures S12 and S13) as the B-spline analysis.
Supporting Information

- A Sellmeier parameterization\(^1,8\) fits \(r_{X^2} = 7.803\) the data at 900-1688 nm as \(n^2(\lambda) = 1 + (B\lambda^2)/(\lambda^2-C)\) where \(B\) and \(C\) are free parameters and \(k = 0\). A determination of \(r_{X^2}\) for the best fit at trial values of \(B\) and \(C\) allows the uniqueness of the result for \(n\) to be tested (Figure S14).

![Figure S11. (a) \(\Psi\) and (b) \(\Delta\) at the center of sample 74141, under three different angles of incidence. The displayed fits are constrained by sharing the optical function (but not the thickness) of the composite layer with 15 other spectra at different locations on the wafer (see the text.)](image)

![Figure S12. (a) real part and (b) imaginary part of the optical function for the composite layer on sample 74141, determined by multi-sample analysis (see the text) using three different parameterizations.](image)
Supporting Information

Figure S13. The absorption coefficient of the Ga\textsubscript{0.66}C\textsubscript{0.10}N\textsubscript{0.24} layer at $\lambda \geq 600$ nm, obtained from fits to the SE data using Kramers-Kronig consistent B-spline and Cody-Lorentz parameterizations for the optical functions. The result by B-splines is reproduced by the Urbach tail in the Cody-Lorentz model, suggesting that the absorption in this spectral region is due to transitions between a band and tail states that arise from disorder in the material\textsuperscript{10}, such as carbon at the interface of the GaN crystals.

Four strategies were employed to prevent correlation in the fit and obtain a unique solution for the layer thickness and the optical functions.

1. Several parameters were known a priori. These were $\theta$, the optical functions of the Si substrate, and the window correction for in-situ measurements. The optical functions of the AlN buffer layer were determined from a reference sample on which only AlN was grown.
2. Variable angle SE (VASE) was performed. Due to interference in the AlN layer, the data at each angle $\theta$ contains new information about the GaN/Ga/C layer\textsuperscript{11}
3. Multi-sample analysis (MSA)\textsuperscript{11} was performed. Ex-situ SE and reflectance data was obtained at 16 locations on the wafer. A single fit of all 16 spectra assumed that they share the same optical function, but have different thicknesses. The validity of this assumption was verified by checking the consistency of the result of fits to limited regions of space, and by comparing the results to MSA for in-situ SE data (datasets at multiple points in time during deposition.)
4. Uniqueness tests were performed for $n$ at 1500 nm (Figure S14), and for the thickness of the composite layer (Figure S15). A uniqueness test consists of a series of fits, each of which fixes the parameter of interest at a value to determine the best possible $r^2$ at that value by varying the remaining parameters. If the resulting “fit landscape” contains a single minimum, this is the unique solution for the parameter under the model.
Supporting Information

**Figure S14.** Uniqueness test for the refractive index at $\lambda = 1500$ nm, in the multi-sample analysis using the Sellmeier parameterization ($900 < \lambda < 1688$ nm) for the optical function of the composite layer on sample 74141.

**Figure S15.** Uniqueness test for the thickness at the center of sample 74141, in the multi-sample analysis using three different parameterizations for the optical function of the composite layer on sample 74141.

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