(V)EELS Characterization of InAlN/GaN Distributed Bragg Reflectors

A Eljarrat1, Ž Gačević2, S Fernández-Garrido2,4, E Calleja3, C Magén3,5, S Estradé1,6 and F Peiró1

1 Laboratory of Electron NanoScopies, LENS-MIND-IN2UB, Dept. Electrònica, Universitat de Barcelona, Spain
2 Instituto de Sistemas Optoelectrónicos y Microtecnología, ISOM, Universidad Politécnica de Madrid, Spain
3 Laboratorio de Microscopías Avanzadas (LMA) - Instituto de Nanociencia de Aragón (INA), and Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Zaragoza 50018, Spain
Email to: aeljarrat@el.ub.es

Abstract. Ten-period InAlN/GaN distributed Bragg reflectors are examined by aberration corrected scanning transmission electron microscopy and by valence electron energy-loss spectroscopy (VEELS) with sub-nanometric spatial resolution and sub-eV energy dispersion. Deconvolution and peak subtraction methods, implemented in Matlab routines, are applied to the low loss region of the obtained VEEL spectra to retrieve information about the band gap energy and chemical composition, whereas a Kramers-Kronig transformation is used to retrieve the complex dielectric function of the examined material. The VEEL measurements reveal significant compositional variations in InAlN layers and show a ~2nm thick InAlN layer with high indium content at each GaN/InAlN interface.

1. Introduction
The high potential of III-nitride semiconductors has been attested by their success in violet/blue lightening. However, high in-plane lattice mismatch between the three binaries (AlN, GaN and InN) is a serious constraint for further progress as it leads to defect formation at heterostructures’ interfaces, affecting detrimentally their (opto)electronic properties. The InAlN ternary compound, with 17-18% indium content, grows in-plane lattice-matched to GaN and opens the possibility for fabrication of strain-free III-nitride heterostructures. Still, several problems remain concerning the growth, crystalline quality and homogeneity of InAlN epitaxial films [1-4]. A precise knowledge of the InAlN...
band gap value and its dependence on In content is a critical issue. Due to ternary composition fluctuations on the nanometer scale, traditional optical techniques used for band gap determination are prone to errors, since they are limited to the micron-range spatial resolution. Aberration corrected scanning transmission electron microscopy (STEM), with sub-nanometric spatial resolution, combined with monochromated electron energy loss spectroscopy (EELS), with <0.2 eV energy resolution, is a promising tool to unravel optoelectronic properties of the novel material. In particular, Valence-Electron Energy Loss Spectroscopy (VEELS), is an excellent technique which focuses on the lower energy loss (low-loss) part of the EEL spectrum (typically <50 eV), that exhibits the most important features regarding the valence and conduction band of the examined material.

2. Experimental

Ten-period nearly lattice-matched InAlN/GaN DBRs, with peak reflectivity around 400 nm, were grown in a RIBER Compact 21 MBE system equipped with a radio-frequency plasma nitrogen source and standard Knudsen cells for gallium, aluminium and indium. A procedure to obtain good quality InAlN/GaN periods with ~18% In content in the InAlN semi period has been described in previous studies [3]. Preparation of the samples for (S)TEM-EELS observation was done in cross-section geometry by polishing down to 50 µm, followed by a dimpling down to 25 µm and a final Ar+ bombardment at V=5kV with an incident angle of 7º using a PIPS Gatan ion mill. TEM experiments were conducted in a JEOL 2010F (S)TEM and in a probe corrected FEI Titan (S)TEM instrument operated at 300 kV with a Wien monochromator and Gatan Tridiem 866 ERS energy filter/spectrometer (collection angle was 17 mrad).

3. Data treatment

Figure 1 illustrates the complete VEELS analysis work-flow carried out on a single raw spectrum. Originated from the elastically scattered part of the electron beam, the zero loss peak (ZLP, see Figure 1a for an example) is used to calibrate the origin of energies of the spectra. The FWHM of the ZLP indicates the energy resolution limit (analogous to an optical system signal widening) of our data: our experimental set-up provided EEL spectrum lines with an energy resolution below 0.2 eV (quantitatively determined using Gaussian fitting of each individual spectrum) and a spatial dispersion of 0.5 nm. Because of low signal-to-noise ratio in low-loss monochromated beam experiments, sometimes, it has been necessary to average 10 spectra (corresponding to about 5 nm of linear displacement). However, when this is done, the spectra are always taken from a homogeneous region far from any interface.

One typical individual VEEL raw spectrum obtained in the GaN layer of the first semiperiod is shown in Figure 1b. Significant information contained in the low-loss regime spectrum can almost be directly examined by naked eye. Besides the ZLP, traces of signals associated with band gap transitions are also noticed. A prominent peak at ~19 eV, the plasmon peak, can be attributed to the collective oscillation of the electrons. The following intensity maxima have been attributed to the presence of the d-band in GaN [5].

Low-loss EELS data processing started with the deconvolution of the ZLP and plural scattering by a Fourier-log routine (according to Egerton [6]). In optimal conditions and with a careful preparation of the spectra for Fourier analysis to obtain best results, the F-log routine will not only separate the ZLP from the rest of the spectrum, but it will also get rid of the part of the signal coming from plural scattering events (through Poissonian modeling). Then, the resulting signal will be the so-called single scattering distribution (SSD, see Figure 1.c), a signal modeled in the theory by Kröger for electron beams traversing thin foils [6].

Before continuing performing transformations on the signal, it is instructive to take a look at the plasmon peak. We can precisely determine the energy and spatial position of the peak through the layers using a peak-fitting procedure to locate the plasmon energy position in an individual spectrum (see Figure 1.d for an example of a Lorentzian peak-fitting procedure in action).
Figure 1. A typical VEELS analysis work-flow, performed on a raw individual spectrum from a GaN layer of one semi-period. These images show the evolution and transformation data from raw untreated spectra in images (a) and (b), to deconvolved spectra in (c) and (d), and finally, calculated complex dielectric functions in (e) and (f).

Once the SSD is identified a small preparation of the signal is enough to perform Kramers-Kronig analysis (KKA) on the spectra assuming the refractive index ($n$) of GaN as a known parameter. We have used $n=2.4$ according to [3]. The case of GaN is clear because its refractive index is known, and will allegedly remain constant in the layer. In the case of InAlN the choice of $n$ is not so clear because of the suspected presence of In segregation in the layer [3], so this is why a GaN example spectrum is presented. In Figure 1.e the energy-loss function (ELF, $\text{Im}(-1/\varepsilon)$), along with its KK-complementary function $\text{Re}(1/\varepsilon)$, are shown. This $\varepsilon$ represents the complex dielectric function (CDF) of the material (part of which is portrayed in Figure 1.f); KKA makes it possible to use $n$ to make a measurement of the foil thickness, and then use Kröger’s equation to separate the ELF. Through Fourier analysis it
then computes the KK transformation, retrieving the full CDF of the material. This iterative process will also deal with the surface-loss signal, leaving only the bulk features in the final result.

From Vegard’s Law we know that for a ternary alloy like InAlN, the lattice constant is related to the ratio of the materials through a linear law (with or without a parabolic bowing term). Using the fact that the plasmon frequency for crystalline materials is also related to the lattice constant, if we precisely determine the energy and spatial position of the peak through the InAlN layer (using our peak-fitting routine) we shall be able to calculate the indium ratio through simple fitting of the plasmon energies for each spatial position to this equation (see Figure 3),

\[ E_{p_{InAlN}} = \delta \cdot E_{p_{InN}} + (1 - \delta) \cdot E_{p_{AlN}} - b \cdot \delta (1 - \delta), \]  

in which \( \delta \) is the In ratio and the \( E_p \)'s are the plasmon energies for binary components InN and AlN (15.7 and 21.1 eV, respectively) and measured for InAlN, \( b \) is the bowing parameter which is adjusted to obtain a mean In ratio equal to the 18% nominal one (\( b = -3.1 \text{eV} \)).

The resulting ELF and CDF contain very valuable information about optoelectronic properties of the bulk material in the sample which can be compared with optically measured ones. Transitions on the electronic band structure of the bulk material related with its crystalline structure appear clearly as discernible features in these functions. The ELF is directly related to the joint density of states between the valence and conduction bands, a magnitude which can be modelled and calculated theoretically by ab-initio computer simulation. In this line, the analysis presented here has been extended to relate optoelectronic and structural properties presented in latter publications [1-3], through band-gap determination, plasmon peak related indium ratio and Cole-Cole plots of CDF.

![Figure 2](image1.png)  **Figure 2.** Plasmon peak evolution along the line displayed in the HAADF micrograph (inset) which suggests the existence of an In rich layer.

![Figure 3](image2.png)  **Figure 3.** Indium excess concentration showing accumulation of InN in the borders of the InAlN layer.

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