

## Strain Modification of GaN in AlGa<sub>x</sub>N/GaN Epitaxial Films

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We investigated AlGa<sub>x</sub>N/GaN heterostructures grown by metal-organic vapor-phase epitaxy on sapphire by calorimetric absorption, transmission and reflection spectroscopy (CAS/CTS/CRS) at 47 mK. The AlGa<sub>x</sub>N film on a 2- $\mu$ m-thick GaN layer introduces additional compressive strain into the GaN layer. A blue shift of the A- and B-exciton line positions is directly proportional to the AlN molar fraction in the films. The amount of strain in the GaN layers is quantified by micro-Raman experiments. We can explain the results by taking into account the elastic properties of GaN and AlGa<sub>x</sub>N.

KEYWORDS: AlGa<sub>x</sub>N, GaN, stress and strain, heterostructure

### 1. Introduction

In the heteroepitaxial growth of GaN on sapphire or SiC substrates, a low-temperature deposited-AlN or GaN buffer layer plays an important role. It provides nucleation centers necessary to realize two-dimensional growth, and allows one to obtain smooth film surfaces free of cracks. Strain is induced in the epitaxial films by thermal mismatch, i.e., the difference in thermal expansion coefficient between GaN and the substrates, rather than by lattice mismatch. Strain modifies the splitting in the valence band and leads to a shift of the free exciton states. They originate from three different valence band states, and are commonly labeled A, B, and C. For GaN epitaxial films on sapphire, the free exciton transitions are blue-shifted, which is caused by the biaxial compressive strain.<sup>1)</sup>

In order to realize electronic and optoelectronic devices such as field-effect transistors or light-emitting diodes, heterostructures of ternary nitrides InGa<sub>x</sub>N and AlGa<sub>x</sub>N are sandwiched between GaN layers. If they can be grown coherently on GaN, the ternary layers are either under tensile (AlGa<sub>x</sub>N) or compressive (InGa<sub>x</sub>N) stress. We will demonstrate that the strained AlGa<sub>x</sub>N films introduce additional compressive strain into the underlying GaN. Using the elasticity theory, we will make comparisons with the experimental results based on photoluminescence, reflection and Raman experiments.

### 2. Experiments

The films were grown by metal-organic vapor phase epitaxy on sapphire (0001) substrates using a low-temperature-deposited AlN buffer and were undoped. Al<sub>x</sub>Ga<sub>1-x</sub>N films with thicknesses between 330 and 740 nm were grown on a 2- $\mu$ m-thick GaN film. The AlN molar fraction varied between  $0 \leq x \leq 0.22$ . More details especially about the determination of the composition can be found in ref. 2. From X-ray measurements, it was shown that the AlGa<sub>x</sub>N films grew coherently on GaN, i.e. the lattice constants were identical within experimental accuracy. For further optical properties, see ref. 2.

In calorimetric absorption spectroscopy (CAS) experiments, one measures the increase in temperature of the sample as a function of the exciting photon energy. The enhancement in sensitivity is due to the fact that the heat capaci-

ty of the sample changes with  $T^3$ ; hence the measurements are conducted at a temperature  $T = 47$  mK. Calorimetric reflection spectroscopy (CRS) and calorimetric transmission spectroscopy (CTS) are spectroscopic techniques which detect the absorption induced by heating of a blackbody.<sup>3)</sup> As a light source in the ultraviolet spectral range, a dye laser pumped by an excimer laser is used. It has a spectral resolution of 50  $\mu$ eV. Raman experiments were performed on a Dilor LABRAM single-grating spectrometer at room temperature. Photoluminescence experiments were conducted at 6 K using a HeCd laser as an excitation source.

### 3. Results

In Fig. 1 we present CAS, CRS and CTS spectra of a sample with AlN molar fraction of 0.06. One clearly recognizes the signals from the A- and B-excitons of the underlying GaN at the band-gap energy of around 3.5 eV. At higher energies, the signal from the A-exciton of the AlGa<sub>x</sub>N film can also be seen. Within the context of this paper, the excitonic properties of AlGa<sub>x</sub>N will not be discussed further.<sup>4,5)</sup>

Well-resolved spectra of the A- and B-excitons of the GaN layer could be observed for the whole set of samples independent of the Al content. Their energy positions as a function of the Al content in the top layer are shown in Fig. 2. There is a clear blue shift for both excitons. The energy difference between A and B increases from 9 meV for  $x = 0.06$  to 11 meV for  $x = 0.22$ .

In the photoluminescence experiments, only the A-exciton transition could be resolved and its energy position was determined. The data are in agreement with the calorimetric measurements (see solid circles in Fig. 2). From CAS and photoluminescence measurements, one can conclude that the top AlGa<sub>x</sub>N layer induces additional compressive strain in the underlying GaN film.

The strain modifies via the deformation potentials, the eigen frequency of the phonons which can be measured by Raman spectroscopy. From the shift of the Raman lines in biaxially compressively strained films compared to the unstrained value, the amount of built-in elastic strain can be quantified. Since the polar modes of E1 and A1 symmetry have a directional dispersion, the longitudinal optical (LO) phonons interact with the vibrations of free carriers, and the E2 (low) has only a very small pressure coefficient, the E2 (high) is the only usable mode for determination of the strain.

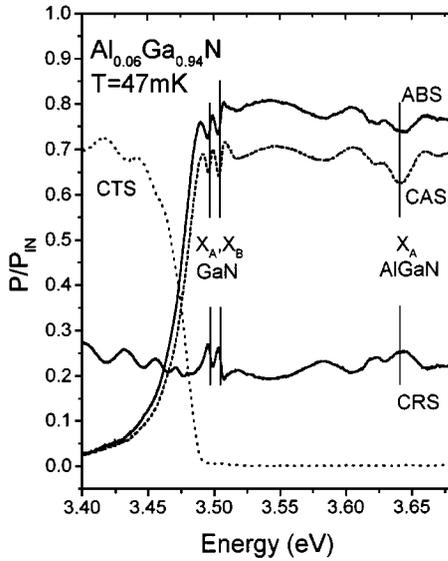


Fig. 1. Calorimetric absorption (CAS), reflection (CRS), and transmission (CTS) spectra of an AlGaIn/GaN heterostructure with AlN molar fraction of 0.06. The structure on the left side (low energy) originates from the underlying GaN film, that at the higher energy side, from the AlGaIn film. For comparison, a usual absorption spectrum (solid line) is included.

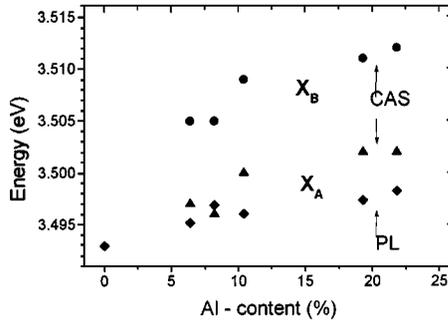


Fig. 2. Positions of the A- and B-excitons in the underlying GaN layers with respect to the Al content of the top AlGaIn layers. Solid circle and triangles: CAS data; solid diamonds: PL data.

Its shift is given by:<sup>6)</sup>

$$\Delta\omega_{E2(\text{high})} = \sigma_{xx} \times 4.2 \text{ cm}^{-1}/\text{GPa},$$

with  $\sigma_{xx}$  the respective component of the strain tensor. We used the room temperature intrinsic value of  $\omega_{E2(\text{high})} = 567 \text{ cm}^{-1}$ , which was determined for free-standing GaN films.<sup>7)</sup> There is a shift of the Raman line in GaN from the intrinsic value as a function of the Al molar fraction in the top layer, as seen in the inset in Fig. 3. It is around  $1.68 \text{ cm}^{-1}$  for  $x = 0.06$  and around  $2.47 \text{ cm}^{-1}$  for  $x = 0.22$ .

In the following, we quantify our results by calculating (see Fig. 4) the in-plane biaxial strain and stress along the [0001] direction for a three-layer system. Layer A with thickness  $d_A$  refers to AlGaIn, layer B with thickness  $d_B$ , to the GaN film and S, to the substrate. For the in-plane biaxial strain, we have:

$$e_{xy} = e_{xz} = e_{yz} = 0 \quad (1)$$

$$e_{xx} = e_{yy} \quad (2)$$

$$e_{zz} = -2 \frac{C_{13}}{C_{33}} e_{xx} \quad (3)$$

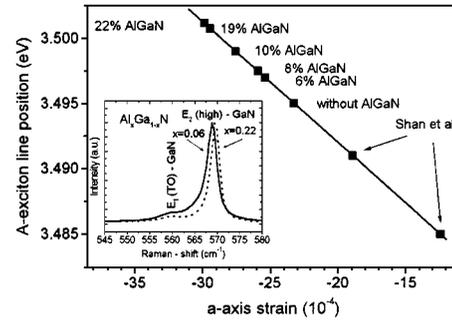


Fig. 3. GaN A-exciton line position versus  $a$ -axis strain for various GaIn layers. The GaIn layers with the AlGaIn layers on top like the one without AlGaIn were  $2\text{-}\mu\text{m}$ -thick, those of Shan *et al.*<sup>9)</sup> respectively thicker. Inset: strain-induced Raman-shift in GaN. The additional Raman shift induced by the AlGaIn layer on top is  $\Delta\omega = 0.8 \text{ cm}^{-1}$ , comparing  $x = 0.06$  with  $x = 0.22$ .

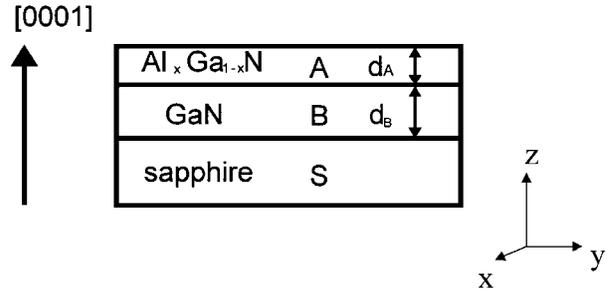


Fig. 4. Schematic layer structure for a three (two)-layer system.

Table I. Calculated values of strain and stress for AlGaIn on GaIn epitaxial films.

	Al <sub>0.06</sub> Ga <sub>0.94</sub> N	Al <sub>0.22</sub> Ga <sub>0.78</sub> N
$a_0$ (Å)	3.1839	3.1718
$\hat{C}$ (GPa)	451.28	454.36
$2C_{13}/C_{33}$	0.510	0.524
in plane		
$a$ (Å)	3.1876	3.1865
$e_{xx}^{\text{AlGaIn}}$ (%)	0.1157	0.4647
$e_{xx}^{\text{GaN}}$ (%)	-0.0430	-0.0778
$e_{zz}^{\text{AlGaIn}}$ (%)	-0.0594	-0.2436
$e_{zz}^{\text{GaN}}$ (%)	0.0219	0.0396
$\sigma_{xx}^{\text{AlGaIn}}$ (GPa)	0.5223	2.1115
$\sigma_{xx}^{\text{GaN}}$ (GPa)	-0.1935	-0.3503
$\sigma_{zz}^{\text{AlGaIn}}$ (GPa)	0	0
$\sigma_{zz}^{\text{GaN}}$ (GPa)	0	0

with  $C_{ij}$  elements of the elastic stiffness tensor with independent components  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ ,  $C_{44}$  and  $C_{66}$ .

$$e_{xx} = \frac{a}{a_0} - 1, \quad (4)$$

with  $a$  as the actual in-plane lattice constant and  $a_0$  that of the unstrained material. For the in-plane biaxial stress we have:

$$\sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0, \quad (5)$$

$$\sigma_{xx} = \sigma_{yy}, \quad (6)$$

$$\sigma_{zz} = 0, \quad (7)$$

Table II. In-plane strain taking into account thermal mismatch and coherent growth of AlGaIn on GaN.

AlN molar fraction	coherent growth (eq. (10))		thermal expansion (eq. (11))		addition	
	$e_{xx,\text{GaN}}$ (%)	$e_{xx,\text{AlGaIn}}$ (%)	$e_{xx,\text{GaN}}$ (%)	$e_{xx,\text{AlGaIn}}$ (%)	$e_{xx,\text{GaN}}$ (%)	$e_{xx,\text{AlGaIn}}$ (%)
0.06	-0.0430	0.1175	0.0083	-0.0083	-0.0347	0.1092
0.22	-0.0778	0.4647	0.0304	-0.0304	-0.0474	0.4343

$$\sigma_{xx} = (C_{11} + C_{12})e_{xx} + C_{13}e_{22}, \quad (8)$$

$$\sigma_{xx} = \hat{C}e_{xx} \quad \text{with} \quad \hat{C} = C_{11} + C_{12} - 2\frac{C_{13}^2}{C_{33}}, \quad (9)$$

In the following, we assume plastic release of the tension in the two-layer system of A and B only. In the first step, we neglect the additional strain which might originate from the difference in thermal expansion between the substrate and layer B, and that the two layers. In this approximation, the state of tension is only determined from the pseudomorphic growth of layer B on A. The in-plane lattice constant is given by:

$$a = a_0^A a_0^B \frac{\hat{C}^A d_A a_0^B + \hat{C}^B d_B a_0^A}{\hat{C}^A d_A (a_0^B)^2 + \hat{C}^B d_B (a_0^A)^2}, \quad (10)$$

The calculated values for the in-plane stress and strain are given in Table I, and the components of the stiffness tensor were obtained by a linear interpolation between the respective values of GaN ( $\hat{C} = 450$  GPa,  $2 \times C_{13}/C_{33} = 0.509$ ) and AlN ( $\hat{C} = 470$  GPa,  $2 \times C_{13}/C_{33} = 0.579$ ),<sup>8)</sup> as was done for the lattice constants (see Table I).

Next we take into account the influence of strain due to the difference in thermal expansion coefficient between layer A and B, using the expression of Volm *et al.*<sup>9)</sup>

$$e_{xx} = \frac{(\alpha_A - \alpha_B)\Delta T}{1 + \alpha_A \Delta T} \quad (11)$$

Assuming a temperature difference between the growth and characterization of  $\Delta T = 1100$  K, one obtains values increasing from  $e_{xx} = 0.008\%$  (for  $x = 0.06$ ) to  $e_{xx} = 0.030\%$  (for  $x = 0.22$ ). However, this is tensile strain in GaN, because GaN has a larger expansion coefficient than AlN.

An addition of both effects, the compressive strain due to the coherent growth of AlGaIn on GaN and the thermally induced tensile strain, still results in compressive strain varying from  $e_{xx} = -0.035\%$  (Al<sub>0.06</sub>Ga<sub>0.94</sub>N) to  $e_{xx} = -0.047\%$  (Al<sub>0.22</sub>Ga<sub>0.78</sub>N). This result is valid for a simple two-layer model and neglects any influence of the substrate (see Table II).

One notes that in all cases the AlGaIn film is under tensile strain, but the GaN layer is under additional compressive strain. In order to quantify it, we compare the line position of the A-exciton with the results from Shan *et al.*<sup>10)</sup> We also include the strain value for a 2- $\mu\text{m}$ -thick GaN film, i.e., as a reference for the A-exciton line position without the influence of an AlGaIn film on top (in such a way that the thermal mismatch cancels out). From  $x = 0$  to  $x = 0.22$ , the axial strain in GaN increases by  $7 \times 10^{-4}$ , whereas the calculated value

is  $1 \times 10^{-3}$ , which is in very good agreement.

The in-plane stress in GaN, on the other hand as monitored by Raman measurements gives a shift of  $0.8 \text{ cm}^{-1}$  for  $x = 0.22$  as compared with the sample with  $x = 0.06$  (see inset in Fig. 3). From calculation one can expect  $\Delta\omega = 0.66 \text{ cm}^{-1}$ . This shows that the simple two-layer model can account for the experimental findings.

#### 4. Summary

In conclusion, we reported on photoluminescence, calorimetric spectroscopy and Ramanspectroscopy of Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures with alloy compositions of  $0 < x < 0.22$ . It was shown that coherently grown AlGaIn layers on top of a GaN layer introduce additional compressive strain into the underlying GaN layer. The experimental results from exciton line position and strain induced Raman shift could be confirmed by calculations using the elasticity theory.

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