Phonon deformation potentials in hexagonal GaN

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In the first part of this paper, we review the deformation potentials of the E_2 and $A_1(LO)$ phonons of hexagonal GaN proposed seven years ago, from a Raman study of stained layers. Elastic constants recently published are taken into account, and the optical calibration of strain is corrected. We show that new values of the biaxial pressure coefficients are only 10% higher than their previous determinations, leading to 3.2 cm^{-1}/GPa and to 0.9 cm^{-1}/GPa, for the E_2 and the $A_1(LO)$ modes, respectively. In the second part, we present another experimental determination of deformation potentials for these phonons. For the present study, a set of undoped epitaxial GaN layers grown on silicon by molecular beam epitaxy has been investigated by means of Raman scattering and x-ray diffraction. Values deduced from these measurements are compared to existing data. On the one hand, the Raman biaxial pressure coefficient has been found as low as 2.43 cm^{-1}/GPa for the E_2 phonon while its counterpart for the $A_1(LO)$ phonon (1.91 cm^{-1}/GPa) is much higher than its previous determination; this value will be of strong importance to calibrate strains in GaN-based nanostructures.

INTRODUCTION

In recent years gallium nitride has attracted considerable attention because of its use in the fabrication of new devices like UV- and visible-light-emitting diodes, power transistors, and laser diodes. However, available substrates such as sapphire, SiC, ZnO, Si, or GaAs exhibit a large lattice mismatch and a difference in the thermal expansion coefficients, with respect to GaN, which result in various biaxial stresses in the epitaxially grown layers. For example, it is well known that stress is compressive in GaN grown on sapphire, whereas its sign is opposite in GaN deposited on SiC. Concerning the substrate Si, previous papers reported on different signs and magnitudes of strain.[1–4]

This information is usually of high importance to get a quantitative insight into internal piezoelectric fields, which are responsible for the redshift of the luminescence energy in strained GaN-AlN nanostructures. Raman spectroscopy is a tool frequently used to determine internal strains and stresses in semiconductor heterostructures, once the phonon deformation potentials of the material under study are known. In fact, experimental and theoretical determinations of these parameters are already available for wurtzite GaN, but they present some discrepancies. The E_2 mode seems to be an ideal probe for stress measurements, due to its nonpolar character and to its high scattering cross section in nonresonant conditions; data in the literature are in fair agreement for this phonon.[5,6] However, Raman spectroscopy performed in near-resonant conditions (i.e. under an UV excitation) must be used to probe GaN quantum wells or dots of very small volume buried in AlN or GaAlN; in this case, only the polar $A_1(LO)$ phonon of GaN shows up clearly in Raman spectra, because it is strongly enhanced by the electronic resonance. For the latter vibration mode, deformation potentials have been determined only once[5] and can be considered questionable. Indeed, their estimation could be tricky, due to a possible interaction between the $A_1(LO)$ polar mode and the free carriers gas (in unintentionally doped samples).

In this paper, we provide a correction to be applied to the first determinations of deformation potentials for free electrons[7] and also for both E_2 and $A_1(LO)$ phonons[5] which are observed in Raman experiments performed in the straightforward backscattering geometry perpendicular to the surface, in hexagonal GaN. Then, another evaluation of the latter parameters is deduced by combining x-ray diffraction and Raman spectroscopy measurements on high-quality undoped GaN layers grown by molecular beam epitaxy (MBE) on Si(111). Values found for the $A_1(LO)$ mode are found definitively higher than those already published. Then the present results are compared to available experimental and theoretical data.

REEXAMINATION OF THE OPTICAL CALIBRATION OF INTERNAL STRESS IN EPITAXIAL GaN LAYERS

First let us recall briefly the pionner work published by Gil *et al.*[7] These authors investigated the energies of excitons A, B, and C, previously measured at low temperature on various GaN layers grown by different methods. They showed that energies E_B and E_C of the latter were correlated to the energy E_A of the former. In their original paper they found, from the collected experimental data, the following equation:

TABLE I. Deformation potentials and variation rate of the energy of exciton A for free electrons in hexagonal GaN.

	a	b
a_e (eV)	-8.16	-8.05
b_e (eV)	$+3.71$	$+3.86$
$\dfrac{dE_A}{d\sigma^B}$ (eV/GPa)	0.0155	0.0175

[a]Data from the original work (Ref. 7).
[b]Values corrected using the elastic constants given in Ref. 12.

$$\frac{dE_C}{dE_A} + \frac{dE_B}{dE_A} = 1 + \frac{A}{A+B} = 2.92 \ \text{eV/GPa}, \qquad (1)$$

where A and B were parameters to be determined. Using Eq. (1), they deduced the ratio $A/B = -2.0869$. In addition, they wrote a very simple relation between this ratio and the deformation potentials a_e and b_e for free electrons in GaN:

$$\frac{A}{B} = \frac{a_e}{b_e}. \qquad (2)$$

Moreover, the value of the pressure coefficient $K^H = dE_A/d\sigma^H = 0.42$ meV/GPa for free electrons, determined from optical measurements under hydrostatic pressure σ^H by Camphausen *et al.*,[8] was used. Therefore a second linear equation could be written:

$$K^H = a_e(\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = a_e(2S_{11} + 2S_{12} + 4S_{13} + S_{33}), \qquad (3)$$

where the set of $\{S_{ij}\}$ are the compliance constants, which can be easily deduced from elastic constants.[9] Combining Eqs. (2) and (3) and using for the elastic constants the data taken in Ref. 10, the deformation potentials $a_e = -8.16$ eV and $b_e = +3.71$ eV were deduced. Finally the following linear variation of the energy E_A (expressed in eV) versus a biaxial stress σ^B (expressed in GPa) was found:

$$E_A = E_A(0) + 0.0155\sigma^B. \qquad (4)$$

Equation (4) could be used to deduce the internal stress of GaN layers grown on any substrate from optical measurements at low temperatures.

However, the various values given by Gil *et al.* may be questionable, because data used in their study have been published several years ago. Therefore, our first goal has been to check if different values would be obtained using elastic constants deduced more recently from experimental determinations[11,12] and also from calculations.[13] In Table I, the original deformation potentials published by Gil *et al.*[7] are compared to those we have found using elastic constants given by Polian *et al.*[12] A difference of about 10% is observed. As a consequence, Eq. (4) must be written with a corrected slope,

$$E_A = E_A(0) + 0.0175\sigma^B \qquad (5)$$

if elastic constants from Ref. 12 are used. This new value means that the magnitude of stress in GaN layers evaluated

in Ref. 5 using the previous calibration has been overestimated. We point out that results obtained with other sets of constants taken in Refs. 11 and 13 have been found close to those collected in Table I.

CORRECTION OF PHONON DEFORMATION POTENTIALS OF GaN

Let us turn to the deformation potentials of phonons in GaN. In their original paper giving their first determination, Demangeot *et al.*[5] made use of the optical calibration given by Eq. (4) taken from Ref. 7 and derived the biaxial stress σ^B in a set of strained layers grown on sapphire. From the measured frequency shift $\delta\omega$ of a given phonon, the Raman biaxial pressure coefficient, expressed using the compliance constants,

$$K^B = \frac{\delta\omega}{\sigma^B} = -2a(S_{11} + S_{12}) - 2bS_{13}, \qquad (6)$$

was found to be 2.9 cm^{-1}/GPa and 0.8 cm^{-1}/GPa, for the E_2 (high) and A_1(LO) phonons, respectively. Then, another relation was found from other data published by Perlin *et al.*:[14] Raman scattering experiments performed under hydrostatic pressure σ^H gave the value of the Raman hydrostatic pressure coefficient,

$$K^H = \frac{\delta\omega}{\sigma^H} = -\frac{2a(C_{33} - C_{13}) + b(C_{11} + C_{12} - 2C_{13})}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}, \qquad (7)$$

for each kind of phonon. Using both Raman coefficients K^B and K^H, the deformation potentials a and b were deduced for the E_2 and A_1(LO) phonons. For the former mode, another study by Davydov *et al.*[6] combining Raman and x-ray diffraction measurements gave similar results. However, it must be pointed out that no determination of these data has been published for the A_1(LO) mode after Ref. 5. In addition, recent calculations of phonon deformation potentials by Wagner and Bechstedt[13] gave results different from those of Demangeot *et al.*, specially for the LO phonon. So it seemed useful to check if the use of elastic constants recently published and of the corrected calibration given by Eq. (5) would change significantly values of the deformation potentials and K^B coefficient.

These values are compared with previous experimental[5] and calculated[13] data in Table II. It can be seen that a satisfactory agreement with data of Wagner and Bechstedt is observed neither for the E_2 mode, nor for the A_1(LO) phonon. In view of the key role of the latter mode in resonant scattering particularly, it is necessary to obtain the true value of its Raman biaxial pressure coefficient. Therefore, we decided to determine one more time these phonon deformation potentials by means of study of a strained GaN layers, which would be independent from an optical calibration of stress.

DETERMINATION OF PHONON DEFORMATION POTENTIALS IN GaN

For this purpose, a set of wurtzite GaN layers exhibiting various thicknesses (ranging from 60 nm to 1500 nm) was

TABLE II. Corrected deformation potentials a and b and Raman biaxial pressure coefficient K^B of hexagonal GaN compared with previous experimental and calculated values.

Mode		a	b	c
	a	−818	−793	−742
E_2	b	−797	−821	−715
	K^B	2.7	3.19	2.41
	a	−685	−527	−664
$A_1(LO)$	b	−997	−1660	−881
	K^B	0.8	0.88	1.91

[a]Published in Ref. 5 using the elastic constants of Ref. 10.
[b]Found from experimental data of Ref. 5 using the elastic constants of Ref. 12.
[c]Computed in Ref. 13.

grown on Si(111) in a RIBER Compact 21 MBE system and using ammonia as the nitrogen precursor. First, an AlN buffer layer (40–50 nm) was grown at about 920 °C. The set of growth parameters (mainly growth temperature and growth rate) has been properly adjusted in order to rapidly obtain a layer-by-layer growth of this AlN buffer layer. Then a GaN buffer layer has been grown at 790 °C using a rate of 1 μm/h. However, if we just apply the procedure described above, we observed cracking of the nitride epitaxial layer during the cooling of the sample. Therefore, in order to compensate the extensive stress appearing during the cooling of the sample, a thick (250-nm) high-temperature AlN layer has been deposited on this buffer layer. Finally the top GaN (strained) layer, of thickness ranging between 200 nm and 710 nm, has been grown on AlN.

X-ray diffraction measurements have been performed using a four-circle SEIFERT diffractometer equipped with a double Ge (220) monochromator selecting only the Cu $K\alpha_1$ wavelength (0.15406 nm) of a line focus. Three GaN layers of thicknesses 200 nm, 400 nm, and 710 nm (referenced in the following as samples 1, 2, and 3, respectively) have been investigated by a two-dimensional (2D) mapping around the four equivalent diffraction lines 105, −105, 015, and 0–15, in order to take in account the possible tilt between the reciprocal lattice and the axis of our goniometer. For example, the map of the reciprocal lattice of sample 1, obtained from x-ray diffraction on the (−1 0 5) planes, is shown in Fig. 1. In this case, two distinct maxima of intensity, corresponding to the buffer layer and to the top layer, are clearly observed. In contrast, they are confused for the 400- and 710-nm-thick layers.

We provide in Table III the average of the lattice constants a and c, deduced from the average parameters a^* and c^* of the reciprocal lattice, for the upper (strained) GaN layer and for the underlying (almost relaxed) buffer layer, for samples 1, 2, and 3. In order to determine the corresponding components ε_{xx} and ε_{zz} of the strain tensor, we used the values of lattice constants a_0 and c_0 of relaxed hexagonal GaN determined by Leszcynski et al.:[15] $a_0 = 0.31890 \pm 0.00003$ nm and $c_0 = 0.51864 \pm 0.00002$ nm. The uncertainties in ε_{xx} and ε_{zz} reported in the same table have been estimated by taking into account the error bars of lattice parameters for strained GaN
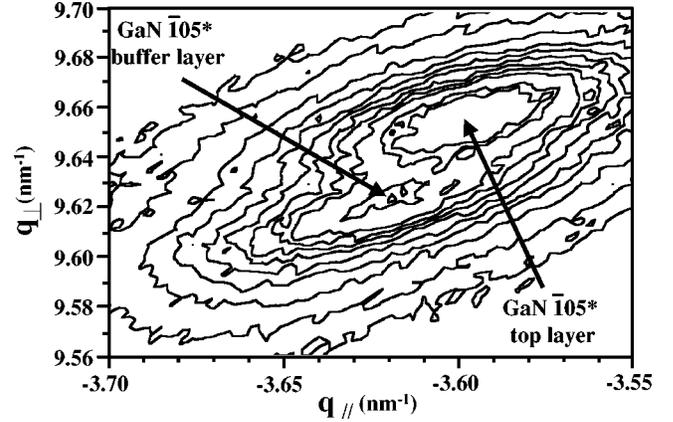
FIG. 1. Map of the reciprocal lattice of the 200-nm-thick GaN layer (sample I), obtained by x-ray diffraction on the (−1 0 5) plane. $q_\perp$ and $q_\parallel$ are the in-plane and z coordinates in the reciprocal space, respectively.

(0.00015 nm and 0.00010 nm, respectively) and for relaxed GaN.[15]

For sample 1, we calculate $\varepsilon_{zz}/\varepsilon_{xx} = -0.45 \pm 0.08$. In fact, this ratio is different from that predicted by the elastic theory if the material would be under pure biaxial stress: in this case, it would be given by $-2C_{13}/C_{33} = R^B$. According to data found by Polian et al.,[12] from Brillouin scattering experiments, $R^B = -0.53 \pm 0.10$ for hexagonal GaN. However, we observe that the expected value of the ratio is included inside the error bars of both x-ray diffraction and Brillouin measurements. We cannot rule out the presence of a weak hydrostatic component of internal strain, which would have an influence on this ratio. In any case, it must be noticed that the method presented in this paper does not need the assessment of a biaxial strain in the layers under study.

Room-temperature micro-Raman spectra of these samples have been recorded in backscattering geometry under a 2.41 eV excitation provided by an Ar^+ laser, using a Renishaw spectrometer. The spot on the surface had a diameter of about 1 μm, and the incident light power on the sample was as low as 1 mW. These experimental conditions prevented a possible local heating of the top layer due to light absorption of the Si substrate, which could affect the mode frequencies. Actually we did not detect any frequency shift of phonons when we slightly increased the power of incident light. Therefore we assume that the frequencies of the E_2 and $A_1(LO)$ modes observed in spectra displayed in Fig. 2 do not

TABLE III. Average values of lattice parameters, strains, and actual R^B ratio, for the three GaN top layers under study.

	a (nm)	c (nm)	ε_{xx} (%)	ε_{zz} (%)	R^B
Sample 1	0.3170	0.5200	−0.60	0.27	−0.45
GaN (200 nm)	±0.00015	±0.0001	±0.056	±0.023	±0.08
Sample 2	0.3180	0.5192	−0.28	0.12	−0.43
GaN (400 nm)	±0.00015	±0.0001	±0.056	±0.023	±0.16
Sample 3	0.3187	0.5186	−0.06	0.01	—
GaN (710 nm)	±0.00015	±0.0001	±0.056	±0.023	
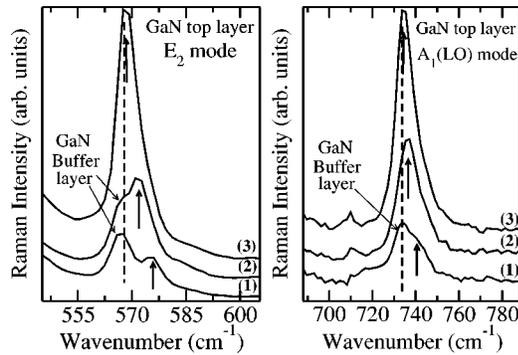
FIG. 2. Micro-Raman spectra of three GaN layers, recorded in backscattering along the *z* axis, for parallel light polarizations, under a 2.41 eV excitation.

TABLE IV. Values of the deformation potentials and Raman biaxial pressure coefficient for the E_2 and $A_1(LO)$ phonons in hexagonal GaN.

		a	b
E_2	a	-850 ± 177	-742
	b	-963 ± 220	-715
	K^B	2.43 ± 0.6	2.41
$A_1(LO)$	a	-782 ± 174	-664
	b	-1181 ± 245	-881
	K^B	1.91 ± 0.58	1.91

[a]Experimentally determined, present work.
[b]Computed in Ref. 13.

need to be corrected from any temperature effect. Besides the contributions of the buffer layer observed near 568 cm^{-1} and 733 cm^{-1}, the features associated with the upper GaN layer are indicated by arrows. They show up clearly for both samples 1 and 2 (but not for sample 3), particularly that associated with the E_2 mode. Experimental values of phonon frequencies used in the following have been extracted from Raman spectra of Fig. 2, using a standard fitting procedure. It is worth noting that we observed simultaneously, for the thinner top layer (sample 1), the larger E_2 frequency difference between the buffer layer and the top layer and two distinct reflexes in the lattice reciprocal map, as seen in Fig. 1. In addition we point out that, for this sample, both the E_2 mode frequency (567 cm^{-1}) and the lattice parameter *a* (0.319 nm) reveal that the GaN buffer layer is under a slight extensive stress. The frequency of the E_2 and $A_1(LO)$ phonons from the top layer depends on the thickness (i.e., the strain) of the film. The frequency shift of both phonons with respect to their frequency in unstrained GaN (Ref. 16) are positive because the internal strain is compressive in such samples. The shift of a given phonon is given by the usual relation

$$\delta\omega = 2a\varepsilon_{xx} + b\varepsilon_{zz}, \qquad (8)$$

where *a* and *b* are the phonon deformation potentials to be determined. The components of the strain tensor have been already determined from x-ray measurements, for three lay-

ers belonging to the set of samples. Figure 3 shows the measured frequency shift $\delta\omega$ of the E_2 phonon versus the measured in-plane strain ε_{xx}, for the three layers under study. The variation is found to be clearly linear, proving that coherent results have been obtained.

Then we used the linear equation (7), which gives the Raman hydrostatic pressure coefficient K^H in terms of *a* and *b*. For the latter, we chose to use the value recently given by Goni *et al.*[17] Combining both equations (7) and (8), the deformation potentials can be easily derived for the E_2 and $A_1(LO)$ modes. Phonon deformation potentials *a* and *b* obtained using elastic constants from Ref. 12 can be found in Table IV, together with the biaxial Raman coefficient K^B deduced from *a* and *b* using Eq. (6), for both E_2 and $A_1(LO)$ phonons. Realistic uncertainties, also displayed in this table, have been evaluated with the absolute error bars of measured values: in the case of sample 1, they are 0.056% and 0.024% for ε_{xx} and ε_{zz}, respectively. The uncertainty in the measured frequency shift is 0.50 cm^{-1} of the E_2 mode in spectra labeled (1) and (2). The estimated errors bars related to the shift of the E_2 mode in spectrum (3) and of all $A_1(LO)$ modes are 0.75 cm^{-1}, which are larger values extracted from the fitting procedure applied to the rather broad structure observed in Raman spectra.

We have checked that deformation potentials do not depend significantly on the set of elastic constants used—for example, those published by Polian *et al.*[12] In addition, it can be observed that the agreement between our data and those calculated by Wagner and Bechstedt[13] is now quite satisfactory also for the polar $A_1(LO)$ phonon, in contrast with our previous determination. The values of *a* and *b* for the latter mode, published in Ref. 5, are likely due to an high unintentional *n*-type doping and to the low carrier mobility in GaN layers investigated during this study. Indeed an overdamping of the free carrier plasmon led to the decoupling of the plasma oscillation with the LO phonon: thus, the frequency shift of the latter can be underestimated in this case.

FIG. 3. Frequencies of the E_2 and $A_1(LO)$ phonons vs the measured in-plane strain ε_{xx}, for the three GaN top layers under study.

CONCLUSION

In the present paper, we are interested in a reexamination of deformation potentials of electrons and phonons previ-

ously determined for wurtzite GaN. This investigation leads us to calculate with a higher accuracy values of these parameters using various sets of elastic constants recently published. According to this procedure, the Raman biaxial pressure coefficients for both the E_2 and $A_1(LO)$ phonons exhibit an increase of 10%. Then we have carried out another study of phonon properties under biaxial stress, by combining lattice dynamics experiments and structural measurements on a set of thin undoped GaN layers grown on a Si(111) substrate. The latter results confirm the accepted val-

ues for the E_2 mode, while the $A_1(LO)$ phonon parameters exhibits a significant deviation with respect to previous data found in the literature. The use of different sets of elastic constants currently available do not have a strong consequence on the final results. We think that the present data for the $A_1(LO)$ mode will be of high importance in future resonant Raman studies of GaN-based nanostructures, because it is well known that only this phonon is clearly observed in such experiments.

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