Phonons and Free Carriers in a Strained Hexagonal GaN-AlN Superlattice Measured by Infrared Ellipsometry and Raman Spectroscopy

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ABSTRACT

Phonon and free-carrier effects in a strained hexagonal (α) $\{GaN\}_l$-$\{AlN\}_m$ superlattice (SL) heterostructure (l = 8 nm, m = 3 nm) are studied by infrared spectroscopic ellipsometry (IRSE) and micro (μ)-Raman scattering. Growth of the heterostructures was performed by metal-organic vapor phase epitaxy (MOVPE) on (0001) sapphire. An unstrained 1 μm-thick α-GaN layer was deposited prior to the SL. SL phonon modes are identified combining results from both IRSE and μ-Raman techniques. The shift of the GaN-sublayer phonon modes is used to estimate an average compressive SL stress of σ_{xx} ~ - 4.3 GPa. The IRSE data reveal a free-carrier concentration of n_e ~ $5\text{x}10^{18}$ cm^{-3} within the undoped SL GaN-sublayers. According to the vertical carrier confinement, the free-carrier mobility is anisotropic, and the lateral mobility ($\mu_\perp$ ~ 400 cm^2/Vs, polarization $E\perp c$-axis) exceeds the vertical mobility ($\mu_\parallel$ ~ 24 cm^2/Vs, $E\|c$) by one order of magnitude.

INTRODUCTION

Strain plays an important role for group-III nitride materials because of large lattice mismatch between binary alloys, and most substrate materials available so far [1]. A possible way to overcome difficulty in growth of high-quality GaN/$Al_xGa_{1-x}N$ heterostructures may be the growth of superlattice (SL) structures with few Angstrom periods. Such SL's may be highly strained. If the SL period remains within the critical thickness of the SL constituents, the stacked {GaN}-{$Al_xGa_{1-x}N$} sublayers should form tensile and compressive stressed "barriers" and "wells" within the SL, and adopt a common in-plane lattice constant. Besides strain-induced shift of SL phonon modes and band-gap energies, the $Al_xGa_{1-x}N$ sublayers should act as barriers and confine free carriers to the GaN sublayers. These carriers should then behave similarly to a two-dimensional carrier gas because of the mobility confinement perpendicular to the SL interfaces.

Gleize *et al*. have recently studied a strained GaN-AlN-SL with average Al concentration of 48% using μ-Raman investigations [2]. The SL was grown by mole-cular beam epitaxy. The authors observed strain-induced shifts of the GaN-sublayer phonon modes, but no free-carrier effects were detected. An estimate for the in-plane strain, ϵ_{xx},

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and the average biaxial stress, σ_{xx}, was given using elastic constants (C_{ij}), and phonon deformation potential constants (a_λ, b_λ) for α-GaN given in Refs. [3] and [4], respectively.

Spectroscopic ellipsometry (SE) is known to be an excellent technique for measurement of thin-film optical properties. Successful application of infrared (IR) SE for measurement of phonon and free-carrier effects in group-III nitride heterostructures was reported previously [5,6]. SE is an indirect technique, and calculated model spectra need to be fit to experimental data. If appropriately chosen, model parameters, which parameterize the dielectric functions of the sample constituents, can provide physically meaningful quantities, such as transverse-optical (TO), longitudinal-optical (LO) frequencies and broadenings, static or high-frequency dielectric constants, and layer thickness. Because free-carrier absorption affects the IR dielectric response, concentration and mobility parameters can be extracted from the IRSE lineshape analysis if the carrier effective mass is known [7]. When combined with electrical Hall measurements, the IRSE data can further provide information about the effective mass parameter, as recently demonstrated for *n*- and *p*-type α-GaN [6].

The focus of this work is to investigate stress and free-carrier effects in a strained α-GaN-AlN-SL by measurement of the long-wavelength dielectric response using IRSE for the first time, in combination with μ-Raman investigations.

EXPERIMENTAL

One SL with 16 periods of alternating wurtzite GaN (8 nm) and AlN (3 nm) layers was grown by MOVPE on (0001) sapphire. A 1-μm-thick GaN layer was deposited on a ~15 nm AlN buffer layer prior to the SL (for more details see Ref. [8]). The sample was measured at room temperature by IRSE and polarized μ-Raman scattering. Ellipsometric parameters were acquired at multiple angles of incidence (57°, 72°), and for wavenumbers from 333 cm^{-1} to 1200 cm^{-1}. A rotating-polarizer, rotating-compensator, Fourier-transform-based variable-angle-of-incidence spectroscopic ellipsometer was used. A detailed description of the IRSE approach is given in Refs. [5,7] and references therein. The μ-Raman spectra were recorded with a XY-Dilor spectrometer at five different configurations in backscattering geometry for wavenumbers from 200 cm^{-1} to 1200 cm^{-1}. The excitation wavelength was 488 nm (Ar^+ laser). The incident laser light power was 150 mW. The diameter of the laser focus at the sample surface was typically 1 μm. The sample orientations during Raman and IRSE measurement are shown in Figs. 1b, and 2b, respectively.

DISCUSSION

Fig. 1a shows the μ-Raman spectra in five different backscattering configurations. The spectra reveal the A_1(TO), E_1(TO) (labeled by “1”, and “2”, respectively), and E_2, A_1(LO), and E_1(LO) phonon modes of the 1-μm-thick GaN layer which supports the SL.

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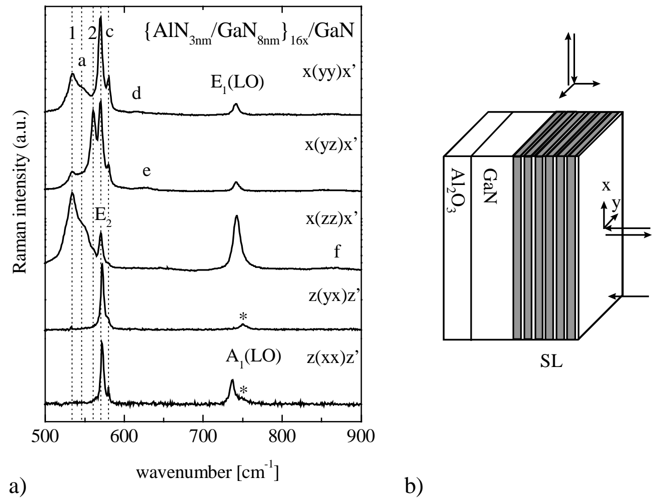

Figure 1. a) Room-temperature μ-Raman spectra recorded in different backscattering configurations from the AlN-GaN-SL sample (sapphire modes are marked by asterisks). b) Sample setup and directions used for the Porto notations.

The phonon frequencies are summarized in Table I. For convenience, we follow the same notation as used by Gleize *et al.*, and label the additional Raman features within Fig. 1a. at 549, 580, 616, 630, and 860 cm^{-1} by *a*, *c*, *d*, *e*, and *f*, respectively [2]. By changing the position of the Raman beam focus from the sapphire interface toward the sample surface we observed that all of these features are due to the SL. The most prominent line is *c* at 580 cm^{-1}, which obeys the symmetry behavior of an E_2 mode. Its frequency is close to that of the thick GaN layer. A very similar line was observed by Gleize *et al*. at 587 cm^{-1}, and was identified as the GaN-sublayer E_2 mode. We also assign *c* to E_2 of the SL GaN-sublayers. The Raman signal *a* could belong to a transverse mode with A_1 symmetry. No clear assignment was done in Ref. [2]. A possible origin for this mode might be the A_1(TO) phonon of the AlN-sublattice, but further proof is necessary at this point. Note that we miss the feature labeled *b* in Ref. [2]. This line was assigned as the SL GaN-sublayer E_1(TO) frequency. As will be discussed below, according to our SL E_2 mode observation at 580 cm^{-1}, the SL E_1(TO) mode should appear ~570 cm^{-1}, and could therefore be subsumed into the strong E_2 Raman feature of the thick GaN layer at 570 cm^{-1}. The feature labeled *d* (616 cm^{-1}) was observed at 620 cm^{-1} in Ref. [2]. It was suggested that this mode may belong to interface excitations. The Raman signal *e* at 630 cm^{-1} in Fig. 1a is identified from the IRSE data analysis as the E_1(TO) phonon of the AlN-sublattice (see below). This mode (*e*) was observed at 635 cm^{-1} in Ref. [2], but not assigned to a particular sample constituent. The broad and weak structure labeled *f* is due to a longitudinal mode with E_1 symmetry. Assignment for this mode from the Raman spectra alone is difficult. However, the IRSE analysis proves that this mode belongs to the high-frequency coupled LO-plasmon-phonon (LPP$^+$) mode of the SL GaN-sublayers. The corresponding LPP$^+$ mode with A_1

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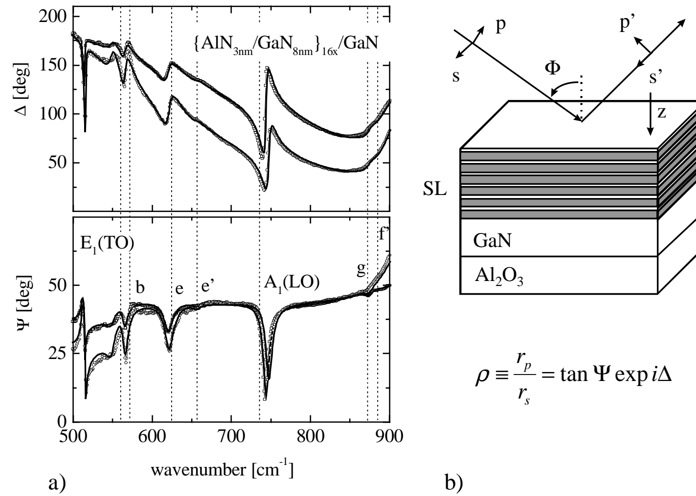

Figure 2. IRSE data (symbols: experiment; solid lines: best fit) at 57° ( ) and 72° ( ) angle-of-incidence Φ from the AlN-GaN-SL sample. b) Sample setup for the ellipsometric measurement, and definition of Ψ and Δ. r_p and r_s are the complex reflection coefficients for parallel (p) and senkrecht (s) polarized light.

symmetry is not observed because of the strong damping of this axial mode due to the vertical confinement of the carriers to the GaN-sublayers (see discussion below).

Fig. 2a presents the IRSE data together with the best-fit model calculation. As discussed somewhere else in detail ([5,6,9]) for wurtzite III-nitride films on *c*-plane sapphire, the IRSE data provide less sensitivity to transverse modes with A_1 symmetry. A_1(LO) and E_1 (TO) modes can be identified immediately from resonance structures within the spectra (see Fig. 2a). The E_1(LO) modes follow from lineshape analysis of the IRSE data. The best-fit parameters, and those which were not varied during the regression analysis (values in square brackets), are given in Table I. The E_1(TO) and A_1(LO) frequencies of the "thick" GaN layer are marked within Fig. 2a. The best-fit for the corresponding E_1(LO) frequency resulted in 742 cm^{-1}. These results agree excellently with those obtained from the μ-Raman spectra, and compare well with the known α-GaN modes [1]. The IRSE data are not sensitive to the IR-inactive E_2 modes. Hence, the resonance at 570 cm^{-1} (*b* in Fig. 2a) can be immediately identified as the SL GaN-sublayer E_1(TO) mode. Furthermore, the feature labeled *e* in Fig. 1a proves now as a TO resonance (*e* in Fig. 2a). It turns out from the IRSE lineshape model calculations that this resonance belongs to the SL AlN-sublayer system. We therefore assign *e* to the E_1(TO) mode of the AlN-sublayers. The small dip at 875 cm^{-1} (*g*) is further assigned to the A_1(LO) mode of the SL AlN-sublayer system. The weak features at 658 cm^{-1} (*e*') and 880 cm^{-1} (*f*') are identified as the E_1(TO) and A_1(LO) modes of the AlN buffer layer, respectively. Gleize *et al*. [2] used the observed shift of the SL GaN phonon modes to calculate the average biaxial stress σ_{xx} and strain ϵ_{xx} within the SL structure. The elastic coefficients C_{ij} and phonon deformation potential constants (a_λ, b_λ) for α-GaN

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Table I: Phonon mode frequencies of the GaN-AlN-SL in cm^{-1}. Values in square brackets were not varied during the IRSE analysis.

	A_1(TO)	E_1(TO)	E_2	A_1(LO)	E_1(LO)
GaN "buffer"	534^a 534^b	560^a 560^b	570^a	737^a 737^b	742^a 742^b
GaN Sublayer	$-^c$ $[534]^b$	$-^c$ 570^c	580^a	$-^c$ 840^b	860^a 840^b
AlN Sublayer	$(549)^d$ $[549]^d$	630^a 625^c	$-^b$	$-^b$ 875^b	$-^b$ $[880]^b$
GaN^e	531.8^e	559^e	568^e		

^{a}*Raman*
^{b}*IRSE*
^{c}*not detectable*
^{d}*tentative mode assignment*
^{e}*unstrained GaN, from V. Yu. Davydov et al., J. Appl. Phys. 82, 5097 (1997)*

were taken from Refs. [3,4]. Here we find that the GaN-sublayers are subject to an average compressive stress of σ_{xx} ~ - 4.3 GPa if we consider the shift of ~ 11 cm^{-1} for the E_1(TO) mode. This is consistent with the shift of the E_2 mode (~ 12 cm^{-1}, see Table I). The GaN-sublayer A_1(TO) mode should then appear at ~ 537 cm^{-1}. The IRSE data are not sensitive to this mode. Unfortunately, we could not find clear evidence of this mode within our μ-Raman spectra. It might be submerged by the stronger A_1(TO) mode of the thick GaN layer. (Note that the total thickness of the SL is only 176 nm.) If elastic deformation of the SL is assumed, the average strain for the GaN layers can be calculated using the C_{ij}'s. We obtain here ϵ_{xx} ~ - 0.9%, which compares well to the in-plane strain (- 0.65%) when both GaN and AlN-sublayers adopt a common in-plane lattice constant, and if we consider the thickness and the relaxed lattice constants [1] for both constituents. This result suggests that the SL adopts a different in-plane lattice constant than the thick GaN "buffer" layer. We note that Gleize *et al*., who investigated a SL with average Al concentration of 48%, observed a higher strain (-1.3%). This value was also slightly larger than that if a common in-plane lattice constant (-1.1%) is assumed. This might be due to uncertainty of the C_{ij}'s known so far.

As a unique feature of the IRSE technique, the ellipsometry parameters are sensitive to free-carrier affected changes within the dielectric functions of thin films. In this work we observe that the SL GaN-sublayers contain free carriers. In particular, we obtain from the best-fit regression analysis that both LO A_1 and E_1 modes are coupled to plasmon excitations, and that the "zero's" of the GaN-sublayer dielectric functions are shifted to higher frequencies [5,7]. To quantify carrier concentration and mobility values, the effective mass parameter has to be known. We assume that the carriers within the GaN-sublayer system are free electrons, which may originate from the AlN sublayer system, i.e., from interface and defect induced donor states. Similar carrier effects were observed in unintentionally-doped $Al_xGa_{1-x}N$ layers [5]. We further assume an isotropic effective mass, and choose a value of $m^*/m_e = 0.22$. [1] As a result, we obtain a carrier concentration of n_e ~ 5 10^{18} cm^{-3}, and a strongly anisotropic carrier mobility. The lateral (electric field polarization $E \perp c$) mobility $\mu_\perp$ ~ 400 cm^2/Vs exceeds the vertical mobility ($\mu_\parallel$ ~ 24 cm^2/Vs) by more than one order of magnitude. Note that for "thick" films we observe that in

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general $\mu_{\parallel} \geq \mu_{\perp}$ due to the columnar $Al_xGa_{1-x}N$ film growth [1,5,6]. In Ref. [5] we obtained an isotropic mobility of ~ 100 cm^2/Vs for a 535 nm thick $Al_{0.28}Ga_{0.72}N$ film. The SL result suggests that the free carriers are limited in their mobility perpendicular to the SL interfaces. This may find a simple explanation because of the lateral carrier confinement by the AlN-sublayers. The anisotropic mobility further explains why the LPP^+ mode with A_1 symmetry cannot be seen whereas that with E_1 symmetry can be observed within the μ-Raman spectra. It is well known that strong damping of LPP modes hinders their observation by Raman spectroscopy [10].

To summarize, we investigated a GaN-AlN SL structure by IRSE and polarized μ-Raman scattering. We assigned SL phonon modes by combining results from both techniques. The shift of the GaN sublayer phonon modes allowed us to calculate the average biaxial strain within the SL. The so obtained strain value agrees well with the strain if a common SL in-plane lattice constant is assumed. This study shows strong anisotropic optical carrier effects within the GaN-sublayers. The carriers have very high mobility values for movement parallel to the SL interfaces, and are almost confined for movement parallel to the SL growth direction.

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REFERENCES

1. J. W. Orton, Rep. Prog. Phys. **61**, 1 (1998).
2. J. Gleize, F. Demangeot, J. Frandon, M. A. Renucci, F. Widmann and B. Daudin, Appl. Phys. Lett. **74**, 703 (1999).
3. A. Polian, M. Grimsditch and I. Grzegory, J. Appl. Phys. **79**, 3343 (1996).
4. V. Yu. Davydov, N. S. Averkiev, I. N. Goncharuk, D. K. Nelson, I. P. Nikitina, A. S. Polkovnikov, A. N. Smirnov, M. A. Jacobson, and O. K. Semchinova, J. Appl. Phys. **82**, 5097 (1997).
5. M. Schubert, A. Kasic, T. E. Tiwald, J. Off, B. Kuhn, F. Scholz, MRS Internet J. Nitride Semicond. Res. **4**, 11 (1999).
6. A. Kasic, M. Schubert, S. Einfeldt, D. Hommel, unpublished.
7. T. E. Tiwald, J.A. Woollam, S. Zollner, J. Christiansen, R. B. Gregory, T. Wetteroth, S. R. Wilson and A. R. Powell, Phys. Rev. B **60**, 11464 (1999).
8. F. Scholz, V. Härle, H. Bolay, F. Steuber, B. Kaufmann, G. Reyer, A. Dörnen, O. Gfrörer, S.-J. Im, A. Hangleiter, Solid State Electron. **41**, 141 (1997).
9. M. Schubert, T. E. Tiwald and C. M. Herzinger, Phys. Rev. B **61** (March 15. 2000).
10. T. Kozawa, T. Kachi, H. Kano, Y. Taya, M. Hashimoto, N. Koide and K. Manabe, J. Appl. Phys. **75**, 1098 (1994).

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