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Interplay between GaN and AlN sublattices in wurtzite $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys revealed by Raman spectroscopy

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The large frequency shift displayed by the longitudinal optical (LO) phonons $A_1(\text{LO})$ and $E_1(\text{LO})$ when going from GaN to AlN promises an accurate determination of the composition in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ bulk layers by Raman spectroscopy. However, this determination is affected by a large uncertainty for low Al mole fractions ($x < 0.20$), due to the broadened spectral line shape exhibited by these modes. A detailed study of Raman spectra recorded on layers with $x < 0.27$, grown either on sapphire or on silicon substrates, has been performed in order to elucidate the origin of that broadening. The influence on the $A_1(\text{LO})$ line shape of the sapphire substrate modes, compositional inhomogeneities, residual strain, and those effects inherent to the lattice dynamics of ternary alloys, is analyzed. We conclude that the broadening is caused by intrinsic inhomogeneities of the microscopic polarization fields resulting from alloying. This effect is usually obscured in other III–V compounds, such as arsenides or phosphides, due to their considerably lower LO–transverse optical splitting. © 2002 American Institute of Physics. [DOI: 10.1063/1.1478788]

I. INTRODUCTION

Ternary compounds based on nitrides of group-III elements are being widely used as the active zone for optoelectronic devices working in the green-ultraviolet spectral range.¹ Many issues related to their structure at an atomic scale, namely, local strain, space-charge transfer between sublattices, alloy disorder, and possible ordered domains, etc., are still the subject of a great study. In fact, material properties such as lattice dynamics, band structure and band bowing, dominant carrier scattering mechanisms, or even the behavior of chemical species during the epitaxial growth depend, among many others, on those issues.

Lattice dynamics of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ system has been widely studied along the whole compositional range by several authors,² though few works have focused on the range of very low Al contents ($x < 0.15$). In this article, special interest is devoted to this range, where typical morphic effects caused by the alloy are already revealed.

II. EXPERIMENT

The frequency and spectral broadening of the scattered light by zone-center optical phonons have been studied by Raman spectroscopy in undoped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ single layers ($0 \leq x \leq 0.27$), with thicknesses above $0.8 \mu\text{m}$. The layers

exhibit wurzite structure and were grown along their c axis either on sapphire, by low-pressure metalorganic vapor phase epitaxy,³ or on Si (111) substrates by molecular-beam epitaxy.⁴ In order to improve the structural properties the samples include, in most of the cases, an AlN buffer (100–150 Å) between epilayer and substrate. The composition has been determined by electron deflection spectroscopy and x-ray diffraction, with uncertainties below 2%. A typical full width at half maximum (FWHM) of 700 arcs was measured for the (0002) x-ray double diffraction peak in the ω -configuration. The x-ray diffraction pattern of samples with $x = 0.09$ and $x = 0.14$ also revealed an additional small peak, attributed to the residual existence of a sort of superlattice formed by Al-rich layers.⁵ The influence of this residual feature on the off-resonance Raman spectra is expected to be negligible. Good quality metal–semiconductor–metal photodiodes were successfully fabricated on these samples.⁶

Micro-Raman measurements have been performed in backscattering configuration at room temperature. An incident beam at 514.5 nm, well below the fundamental band gap of the material, was focused onto a region of $\sim 1 \mu\text{m}$ diameter, and the scattered light was analyzed through a Dilor triple spectrometer provided with a charge coupled device detector. The spectral resolution is estimated to be $\pm 1.5 \text{ cm}^{-1}$. Either by rotating the incident polarization or tilting the sample, different longitudinal optical (LO) or transverse optical (TO) phonon peaks [A_1 (longitudinal optical)

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FIG. 1. Raman spectra recorded under $z(x',x')\text{-}z$ polarization configuration from $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers. x' is any perpendicular direction to the wurtzite c axis (z). Sample labeled $x=0.02$ was grown on Si(111). The frequency of the $A_1(\text{LO})$ mode in GaN is indicated by the vertical line. The dotted curve represents the estimated contribution of the sapphire E_g mode to the line shape in the sample with $x=0.09$.

(LO), $A_1(\text{TO})$, $E_1(\text{TO})$, E_2] were revealed according to the Raman selection rules for the deformation potential mechanism of this material. In particular, $A_1(\text{LO})$ is allowed in the $z(x',x')\text{-}z$ geometry, where the wurtzite c axis is along z , and x' being any perpendicular direction. The $E_1(\text{LO})$ mode has been also observed in the $x'(z,z)\text{-}x'$ configuration for which it is apparently forbidden, as reported in other works.⁷

III. RESULTS

Figure 1 shows the evolution of the $A_1(\text{LO})$ mode in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ for different alloy compositions. The broad line shape observed in the layers with low Al content ($0.02 < x < 0.14$) is remarkable. This effect has been detected in many works, and is often attributed to the presence of the E_g phonon mode of the sapphire substrate at 750 cm^{-1} .^{7,8} However, spectra taken on layers grown on Si, with nominal Al content $x < 0.10$, show a similar shape, as observed in Fig. 2, thus indicating that this feature is rather intrinsic for the alloy.

Spectra in Figs. 1 and 2 show that either in layers grown on Si or on sapphire, a shoulder appears on the low-frequency side of the main $A_1(\text{LO})$ peak, already for very low Al contents. This feature appears to shift with x , but at a lower rate than the main peak. At $x \approx 0.10$, it spreads over 12 cm^{-1} below the peak. On the other hand, its intensity increases achieving its maximum relative value respect to the main peak at $x \approx 0.10$. Eventually, the shoulder merges into an asymmetrical broadening of the $A_1(\text{LO})$ mode, which is indeed a feature associated with scattering by alloy disorder.⁹

The contribution of the sapphire E_g phonon peak (at 750 cm^{-1}) to that spectral feature may be significant, depending on both epilayer thickness and probing depth. That mode, together with the A_{1g} (at 418 cm^{-1}) were simultaneously detected in a number of spectra from thin layers grown on

FIG. 2. Raman spectra recorded on a set of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers grown on Si. The vertical dashed line indicates the frequency of the $A_1(\text{LO})$ mode in bulk-like GaN.

sapphire. From their comparison, we conclude that the intensity of the E_g mode results approximately one third of that of the A_{1g} , in agreement with other works.¹⁰ Then, taking the intensity of the A_{1g} mode as a reference, the presence of the E_g sapphire peak (750 cm^{-1}) under the $A_1(\text{LO})$ line shape has been estimated (see the dotted curve in Fig. 1). This contribution should not be relevant under our experimental conditions, although it becomes more important in thinner layers (thicknesses below $0.6\text{ }\mu\text{m}$).

The FWHM of the line shapes for the $A_1(\text{LO})$, $A_1(\text{TO})$, and E_2 modes, are plotted versus the alloy molar fraction (x) in Fig. 3, for layers grown on sapphire and Si (111). Data measured by other authors⁷ under similar conditions have also been included. From the graph, we observe that the broadening of the $A_1(\text{LO})$ mode is larger in layers with an Al content around 10%–14% than in layers with

FIG. 3. FWHM (in cm^{-1}) for the Raman line shapes of the $A_1(\text{LO})$, $A_1(\text{TO})$, and E_2 modes measured in bulk $\text{Al}_x\text{Ga}_{1-x}\text{N}$. The dashed curves are guides for the eye.

FIG. 4. Raman spectra recorded in $x'(z,z)-x'$ polarization configuration from bulk $\text{Al}_x\text{Ga}_{1-x}\text{N}$. The frequency of the $E1(\text{LO})$ mode in GaN is indicated by the vertical line. Layers with residual Al content and $x=0.02$ were grown on silicon.

higher Al content. Moreover, this unusual broadening appears to affect only to the longitudinal mode.

In Fig. 4, Raman scattering from the $E1(\text{LO})$ mode is revealed under the $x'(z,z)-x'$ geometry. It should be pointed out that this mode is theoretically forbidden for this polarization configuration, so its presence could be justified by a nonplanar excitation wave front caused by the focusing lens, together with a possible misorientation of some crystalline microstructures.¹¹ In order to evaluate the contribution to $E1(\text{LO})$ scattering from the off-axis radiation introduced by the lens, we have assumed the geometrical theory of light, and integrated the scattered intensity over the illuminated conical region. This model is able to predict, for the f number of our lens, a significant contribution to $E1(\text{LO})$ scattering under $x'(z,z)-x'$ polarization configuration, but a much lower one under $x'(y',y')-x'$ geometry, in agreement with the observations. Similar predictions for the $A1(\text{TO})$ scattering have been checked experimentally. Moreover, this effect does not lead to a significant contribution to $E1(\text{LO})$ scattering under $z(x',x')-z$ configuration. Consequently, the appearance of forbidden scattering can be mainly attributed to our excitation conditions.

In Fig. 4, a low-frequency shoulder as well as a pronounced broadening of the $E1(\text{LO})$ line shape are also observed. The sapphire mode at 750 cm^{-1} is not active in this configuration as checked by illuminating the substrate. Unfortunately, the same reasons which make possible the observation of the $E1(\text{LO})$ mode in this configuration, also apply to $A1(\text{LO})$. In consequence, the shoulder on the low-frequency side can not be unambiguously ascribed to an $E1(\text{LO})$ -like feature.

IV. DISCUSSION

The broadening affecting the $A1(\text{LO})$ and possibly the $E1(\text{LO})$ line shapes could be preliminarily ascribed to intrinsic factors, such as in-band modes arising from different sublattice oscillators within the alloy, or alternatively, to extrinsic factors, namely, compositional inhomogeneities or nonuniform relaxation of built-in strain.

From the point of view of lattice dynamics, the AlGaIn alloy is assumed to exhibit “one-mode behavior”, i.e., only one transverse and one longitudinal phonon are expected along the whole compositional range (for each irreducible representation of the crystal symmetry, $A1$, $E1$). Other modes, which theoretically would exist due to the presence of two sublattices, remain as *in-band* modes. These modes are usually hidden within a “plateau” of disordered scattering between the observed LO and TO bands, and are hardly resolved. However, the observation of these phonons is possible depending on several factors (frequency of the localized modes of the dilute atoms in the pure binary compounds, overlapping of the phonon density of states of the alloy end-members, etc.).¹²

The evolution of the frequency and intensity of in-band modes with x may be roughly described in terms of the random element isodisplacement (REI) model, detailed in Ref. 13. This model takes into account the observed effect that the phonon bands degenerate into the vibrational modes of isolated, substitutional atoms for the case of very dilute solid solutions ($x \approx 0$ or $x \approx 1$). These localized vibrational modes (LVM) of Al in GaN or Ga in AlN determine in part the subsequent evolution of the phonon bands along the compositional range. In case the observed low-frequency shoulder of the $A1(\text{LO})$ phonon were an in-band mode, one can estimate the frequency of the LVMs of Al in GaN (Al_{LVM}) and Ga in AlN (Ga_{LVM}) which would be consistent with the observed evolution. The values obtained imply that the Ga_{LVM} and Al_{LVM} frequencies should fall very close to the respective $A1(\text{LO})$ phonons of AlN and GaN. This is in contradiction to theoretical estimations, which predict that the frequency of Ga_{LVM} should be considerably lower than that of Al_{LVM} , i. e., very far from the $A1(\text{LO})$ band in AlN.^{2,7}

In view of its behavior upon selection rules, and the evolution with x , we believe that the feature at 705 cm^{-1} in Fig. 4, (sample with $x=0.25$) can be one of such in-band modes, which shows up likely from disorder activated TO scattering.

Concerning the extrinsic effects, a nonuniform strain relaxation along the Raman probing depth is known to produce frequency shifts as well as asymmetrical Raman line shapes.¹⁴ However, the residual strain should be of the opposite sign in layers grown on sapphire or on silicon. This should lead to a lateral broadening but on different sides of the main peak, which is in contradiction to our observations.

Evidences of compositional inhomogeneities have been detected in InGaIn -based systems,¹⁵ and invoked to explain the broadening of the $A1(\text{LO})$ mode in Raman spectra from AlGaIn layers.¹⁶ However, such a mechanism should lead to a similar dependence on x of the broadening for the different modes, which disagrees with our observations. Moreover, a

model which assumes a *homogeneous random* distribution of Al atoms in the alloy, namely the “spatial correlation model”,⁹ has been successfully applied to explain the asymmetrical broadening of the nonpolar *E*2 mode along the whole composition range of AlGaIn,¹⁷ in layers grown under similar conditions to the samples under study. This result contributes to discard random compositional inhomogeneities as the main explanation for the unexpected broadening of the A1(LO) polar mode in the range of low Al contents.

Since the broadening appears to affect essentially to the LO modes, we correlate it to the autopolarization field responsible for the *large* LO–TO splitting observed in these materials. That field arises from the dipolar character of the bond between III–V species, and is therefore determined by atomic displacements and bond effective charges ($e_{0\text{ GaN}}^*, e_{0\text{ AlN}}^*$). The bond effective charge is, in turn, subject to space-charge transfers among GaN and AlN sublattices in the alloy.^{12,18} In general, a local redistribution of charge among Al–N and Ga–N bonds is induced by the different ionicity of Al and Ga, and by local lattice distortions due to their different bond lengths. As a result, ternary compounds eventually behave as a matrix of randomly distributed dipoles, with measurable influence on the free carrier mobility, lattice dynamics, etc. This microscopic effect is considered to be responsible for the intense spontaneous and piezoelectric fields observed in III-nitride heterostructures.¹⁹

In view of the deformation potential coefficients for LO and TO modes,²⁰ a direct influence of the local lattice distortions on the frequency of these phonons is expected to be of a similar order, insufficient to explain the observations. However, a dispersion of the bond effective charge, resulting from space-charge transfers via local lattice distortions, should in first approximation affect only to LO phonons.

Within the framework of the REI model proposed in Ref. 13, we have calculated the fluctuation of the bond effective charge necessary to produce a frequency spreading equivalent to the FWHM of the A1(LO) line shape. For that purpose, we have defined a parameter $\lambda(x)$ as the fraction of the Al–N effective charge which is transferred to the GaN bond in $\text{Al}_x\text{Ga}_{1-x}\text{N}$. Thus, the Ga–N effective charge can be expressed by

$$e_{\text{GaN}}^*(x) = e_{0\text{ GaN}}^* + \lambda(x) \cdot e_{0\text{ AlN}}^* \quad (1)$$

where $e_{0\text{ GaN}}^*$ and $e_{0\text{ AlN}}^*$ are the bond effective charges in the corresponding binaries. Since the charge transfer can depend on the composition, a linear variation of λ with x have been assumed, according to the general trends of the model:

$$\lambda(x) = \lambda_0 \cdot x, \quad (2)$$

where λ_0 should fall within $[-1,1]$. Accordingly, a redefinition of the Al–N effective charge is introduced in the model:²¹

$$e_{\text{AlN}}^*(x) = e_{0\text{ AlN}}^* - \lambda_0 \cdot (1-x) \cdot e_{0\text{ GaN}}^* \quad (3)$$

In this way, the dispersion of the bond effective charge is converted into variations of the λ_0 parameter. When applying the foregoing concepts to the experimental results from the

sample with $x=0.10$, we find that a variation $\Delta\lambda_0 \approx 0.5$ is required to justify a frequency spreading of 12 cm^{-1} in the A1(LO) line shape. It is noticeable that a similar variation $\Delta\lambda_0$ in $\text{In}_{0.1}\text{Ga}_{0.9}\text{As}$ would lead to a frequency dispersion $<1\text{ cm}^{-1}$. This result can be extrapolated to those ternary compounds with LO–TO splitting considerably lower than nitrides (most of arsenides and phosphides).

V. CONCLUSIONS

In conclusion, we propose that fluctuations of the charge transferred between the binary-like bonds, usually unnoticed in other III–V compounds, are responsible for the frequency broadening of the LO phonon scattering in AlGaIn. Thus, Raman spectroscopy would be able to provide information on the microscopic distribution of bond effective charges along the compositional range in ternary nitrides. The consequences of this effect on carrier scattering mechanisms and band gap bowing will be the subject of future work.

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¹H. Morkoc, *Nitride Semiconductor Devices*, Springer Series in Material Science Vol. 32 (Springer, Berlin, 1999); B. Gil, *Group III Nitride Semiconductor Compounds. Physics and Applications* (Clarendon, Oxford, 1998); S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997).

²F. Demangeot, J. Groenen, J. Frandon, M. A. Renucci, O. Briot, S. Clur, and R. L. Aulombard, *Appl. Phys. Lett.* **72**, 2674 (1998); C. Bungaro and S. De Gironcoli, *ibid.* **76**, 2101 (2000).

³F. Omnès, N. Marengo, B. Beaumont, Ph. De Mierry, E. Monroy, F. Calle, and E. Muñoz, *J. Appl. Phys.* **86**, 5286 (1999).

⁴M. A. Sánchez, E. Calleja, E. Monroy, F. J. Sánchez, F. Calle, E. Muñoz, and R. Beresford, *J. Cryst. Growth* **183**, 23 (1998).

⁵P. Ruterana, G. De Saint Jores, M. Lügt, F. Omnès, and E. Bellet-Amalric, *Appl. Phys. Lett.* **78**, 344 (2001).

⁶E. Monroy, F. Calle, E. Muñoz, and F. Omnès, *Appl. Phys. Lett.* **74**, 3401 (1999).

⁷F. Demangeot, J. Groenen, J. Frandon, M. A. Renucci, O. Briot, S. Ruffenach-Clur, and R. L. Aulombard, *MRS Internet J. Nitride Semicond. Res.* **2**, 40 (1997); A. Cros, H. Angerer, O. Ambacher, M. Stutzmann, R. Holper, and T. Metzger, *Solid State Commun.* **104**, 35 (1997).

⁸K. Hayashi, K. Itoh, N. Sawaki, and I. Akasaki, *Solid State Commun.* **77**, 115 (1991).

⁹P. Parayanthal and F. H. Pollak, *Phys. Rev. Lett.* **52**, 1822 (1984).

¹⁰Z. C. Feng, M. Schurman, and R. A. Stall, *J. Vac. Sci. Technol. A* **15**, 2428 (1997).

¹¹S. D. Hersee, J. C. Ramer, and K. J. Malloy, *MRS Bull.* **22**, 45 (1997).

¹²G. Landa, R. Carles, and J. B. Renucci, *Solid State Commun.* **86**, 351 (1993).

¹³E. Jahne, *Phys. Status Solidi B* **74**, 275 (1976); E. Jahne, *ibid.* **75**, 221 (1976).

¹⁴A. L. Alvarez and F. Calle, *Defect Diffus. Forum* **159**, 211 (1998).

¹⁵D. Behr, J. Wagner, A. Ramakrishnan, H. Obloh, and K.-H. Bachem, *Appl. Phys. Lett.* **73**, 241 (1998).

¹⁶M. Yoshikawa, J. Wagner, H. Obloh, M. Kunzer, and M. Maier, *J. Appl. Phys.* **87**, 2853 (2000).

¹⁷L. Bergman, M. D. Bremser, W. G. Perry, R. F. Davis, M. Dutta, and R. J. Nemanich, *Appl. Phys. Lett.* **71**, 2157 (1997).

¹⁸G. P. Srivastava, J. L. Martins, and A. Zunger, *Phys. Rev. B* **31**, 2561 (1985).

¹⁹D. Jena, A. Gossard, and U. K. Mishra, *J. Appl. Phys.* **88**, 4734 (2000).

²⁰J.-M. Wagner and F. Bechstedt, *Appl. Phys. Lett.* **77**, 346 (2000).

²¹Notice that the linear-chain model weights each effective charge, e_{GaN}^* , e_{AlN}^* , by its molar fraction, $(1-x)$ or x respectively, so the charge transferred between sublattices is equivalent.