Investigation of optically active E_1 transversal optic phonon modes in $Al_xGa_{1-x}N$ layers deposited on 6H–SiC substrates using infrared reflectance

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We report an investigation, performed in the full composition range $x=0-1$, of the change in infrared reflectivity spectra of $Al_xGa_{1-x}N$ layers deposited on 6H–SiC substrates. We have found two different transverse E_1(TO) phonon frequencies that can be assigned to AlN-like and GaN-like modes. The composition dependences of these frequencies can be well approximated by linear functions and the oscillator strengths scale like the corresponding Al and Ga mole fractions, respectively. On a purely experimental basis, this establishes evidence of a two-mode behavior for this controversial alloy system. The frequencies of the impurity mode of Ga in AlN (622 cm^{-1}) and of the impurity mode of Al in GaN (643 cm^{-1}) were determined. © *1998 American Institute of Physics.* [S0003-6951(98)00639-1]

$Al_xGa_{1-x}N$ is a well-known material, not only for optoelectronic device applications in the ultraviolet range but also because it offers interesting opportunities for high-power, high-temperature, and high-frequency electronic devices. However, up to now, the knowledge of the most fundamental properties of $Al_xGa_{1-x}N$ is still relatively poor and, in particular, little is known about the vibrational properties of this alloy in the full composition range.

$Al_xGa_{1-x}N$ is a wurtzite-type crystal with four atoms per unit cell. In such crystals there are nine optical modes which, at the center of the Brillouin zone, reduce to the Raman active E_2 mode, infrared and Raman active A_1 and E_1 modes, and the silent B_1 mode. Most of the information on $Al_xGa_{1-x}N$ vibrational properties is based primarily on Raman experiments collected in the backscattering configuration[1–3] and focused mainly on the A_1(LO) [longitudinal optic (LO)] and E_2 mode frequencies. However, these experiments are not so easy to interpret, especially when a partial or complete relaxation of the selection rules occurs, in which case the normally forbidden B_1 mode may also appear.[2] Moreover, the traditionally used sapphire substrates always display a complex phonon structure in the same spectral range. All these factors make any unambiguous assignment of the Raman data difficult. As a consequence, up to now, a one-mode behavior was reported for the A_1(LO) and A_1(TO) [transversal optic (TO)] frequencies[1,3] as well as the E_1(TO) and E_1(LO) ones.[2] Conversely, the E_2 mode was claimed to exhibit a two-mode behavior.[2,3]

Such a comportment is hard to understand. For cubic materials, the existence of a local end-gap mode, if one of the components is infinitely diluted,[4] the relative energetic positions of the reststrahlen bands in the pure materials,[5] or the mass ratios of common and mixed components,[6] sometimes allow us to predict the behavior of phonons in alloys. To the best of our knowledge, there is no general criterion which would allow us to predict the phonon behavior of mixed crystals with wurtzite symmetry.

The primary objective of this work was to check, on a purely experimental basis, the composition dependence of long-wavelength TO phonon modes in $Al_xGa_{1-x}N$, and toward this end, we chose to investigate the infrared reflectivity spectra of relatively thin (submicrometer-size) epitaxial layers deposited on 6H–SiC. In this case, only the E_1-like TO modes should manifest (see Fig. 1) themselves and should give sharp maxima in the reflectivity corresponding to TO phonon frequencies. They are superimposed on a large SiC substrate background, which is much simpler than the sapphire one.

The epitaxial layers of $Al_xGa_{1-x}N$ were deposited on ⟨0001⟩-oriented 6H–SiC substrates in a cold-wall, vertical, radio-frequency (rf) inductively heated OMVPE (organometallic vapor-phase epitaxy) reactor, at 45 Torr and a temperature between 1050 and 1150 °C. Triethylgallium (TEG), triethylaluminum (TEA), and ammonia (NH_3) diluted in H_2 were used as source materials. In the case of $Al_{0.12}Ga_{0.88}N$, a thin (800 Å thick) AlN buffer layer was also deposited. The structural, microstructural, optical, and electrical properties of the samples have been previously analyzed using different techniques. The results have been reported elsewhere.[7] The only important point to notice is that the layer composition (x) was determined by energy-dispersive x-ray spectroscopy (EDX), atomic-emission spectroscopy (AES), and Ruther-

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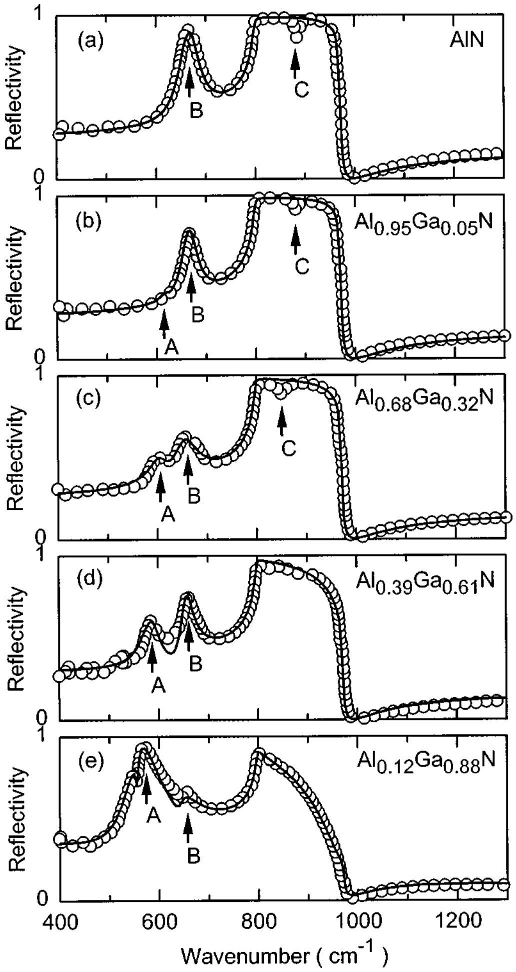

FIG. 1. Infrared reflectivity spectra: experimental results (circles) and fitted spectra (solid line). Arrows marked A, B, and C correspond to $E1$(TO) GaN-like, AlN-like, and LO modes, respectively.

ford backscattering spectrometry (RBS) with good overall agreement.

We have collected the infrared reflectivity spectra at room temperature. We used nonpolarized light and a fourier transform spectrometer, equipped with a KBr beam splitter and a mercury–cadmium–telluride detector cooled down to 77 K. We worked in a quasinormal incidence, with the propagation vector being parallel to the *c* axis (the maximum incidence angle was $\sim 12°$). In many cases, Fabry–Perrot oscillations coming from multiple intralayer reflections were visible. They appeared mostly in the spectral range 1500–8000 cm^{-1}, where all $Al_xGa_{1-x}N$ films were transparent. Taking the refractive index of $Al_xGa_{1-x}N$ from the work of Ambacher *et al.*,[8] we have used these interference data to determine the layers' thickness. We have obtained the following values: AlN, 0.22 μm; $Al_{0.95}Ga_{0.05}N$, 0.15 μm; $Al_{0.68}Ga_{0.32}N$, 0.2 μm; $Al_{0.39}Ga_{0.61}N$, 0.25 μm; and $Al_{0.12}Ga_{0.88}N$, 0.6 μm.

A summary of experimental results obtained on the five $Al_xGa_{1-x}N$ samples is presented in Figs. 1(a)–1(e). Thanks to our special experimental configuration (using SiC substrates and thin $Al_xGa_{1-x}N$ layers), we resolve four phonon structures unambiguously: (i) the broad band, located between 800 and 1000 cm^{-1}, corresponding to the SiC reststrahlen band; (ii) two large peaks, labeled A and B at lower energy; and (iii) the sharp feature labeled C, in the SiC reststrahlen band.

Generally speaking, the composition dependence of the long-wavelength optical phonons in a mixed crystal can exhibit either a one-mode or two-mode behavior.[6] In crystals with a one-mode behavior, the phonon frequency varies approximately linearly with composition, between the limiting frequencies of the two binary crystals, while the oscillator strength stays approximately constant. Examples of such crystals are $GaAs_{1-x}Sb_x$ (Ref. 9) or $Zn_{1-x}Cd_xS$.[10] Conversely, in mixed crystals with a two-mode behavior phonon frequencies characteristic of the pure binary crystals can be observed (almost unchanged) in the full composition range. The phonon frequencies are very close to those of the pure crystals and the oscillator strength of each mode scales, approximately, like the mole fraction of the binary material in the alloy. Examples of such crystals are $InP_{1-x}As_x$,[11] $ZnS_{1-x}Se_x$,[12] or $Al_{1-x}Ga_xAs$.[13,14]

Clearly, our experimental results suggest that the two peaks labeled A and B are associated with two different E_1(TO)-like frequencies. Indeed, with increasing Ga composition, the B peak of Fig. 1(a) weakens, the second peak (A) appears, and the intensity is transferred from B to A. At the same time, we find only one clear structure (labeled C) for the LO mode. It appears on the background of the SiC reststrahlen band and, while forbidden in the normal incidence configuration, originates from a finite angle incidence effect.[15] The striking point is that, while shifting toward low energy (lower Al contents), it does not split and seems to be rather of the one-mode type. In other words, simple consideration of the experimental results suggests that the TO and LO phonon frequencies in $Al_xGa_{1-x}N$ exhibit two different behaviors.[16]

In order to interpret the experimental data quantitatively we performed calculations of the reflectivity using a standard transfer matrix method for the multilayer structure. The dielectric function of $Al_xGa_{1-x}N$ was supposed to be the sum of two phonon oscillators and a free-carrier contribution:

$$\epsilon(\omega)=\epsilon_\infty+\sum_{i=1,2}\frac{f_i}{\omega_{\mathrm{TO}_i}^2-\omega^2-i\gamma_i\omega}-\frac{\epsilon_\infty\omega_P^2}{\omega(\omega-i\gamma_{\mathrm{FE}})},$$

where ω_{TO_i}, f_i, and γ_i (with $i=1,2$) correspond to the TO phonon frequencies, oscillator strengths, and damping factors of the GaN-and AlN-like modes, respectively, and ω_P, γ_{FE} correspond to the plasma frequency and damping factor of the free electron gas. These frequencies, oscillatory strengths, and damping factors have been taken as fitting parameters. For the dielectric function of the 6H–SiC substrates and AlN buffer layers we used the following values:

SiC: $\epsilon_\infty=6.52$, $\omega_{\mathrm{LO}}=970\ \mathrm{cm}^1$, $\omega_{\mathrm{TO}}=797\ \mathrm{cm}^{-1}$,

$\gamma=5\ \mathrm{cm}^{-1}$;[17,18]

AlN: $\epsilon_\infty=4.68$, $\omega_{\mathrm{LO}}=894\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{TO}}=664\ \mathrm{cm}^{-1}$,[19]

$\gamma=50\ \mathrm{cm}^{-1}$.

The results of fits are compared with experiments in Fig. 1. Since the corresponding structures are very clearly resolved in the experimental spectra, the two different transverse phonon frequencies can be obtained with good preci-

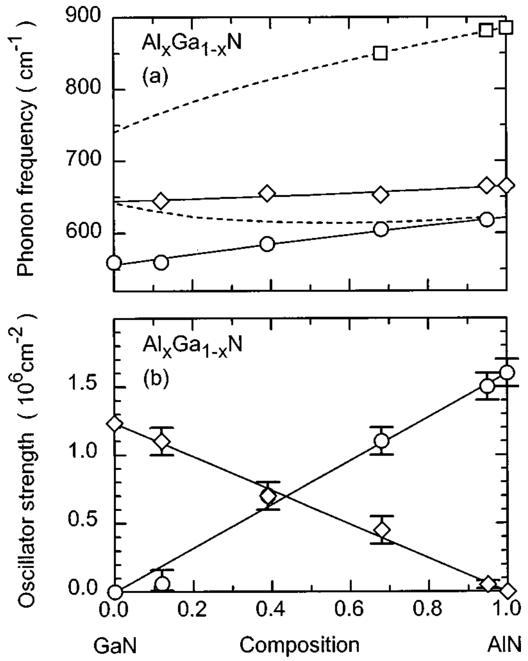

FIG. 2. (a) The composition dependence of phonon mode frequencies in $Al_xGa_{1-x}N$: circles, AlN-like TO mode; diamonds, GaN-like TO mode; and squares, LO mode. Solid lines represent the linear fit to the experimental points. Dashed lines correspond to calculated frequencies of LO modes, the peak positions of $\mathrm{Im}[\epsilon^{-1}(\omega)]$. (b) The composition dependence of oscillator strength of AlN-like (circles) and GaN-like (diamonds) phonon modes in $Al_xGa_{1-x}N$. Solid lines represent the linear fit to the experimental points.

sion. This is because we have chosen to investigate very thin layers for which the broad $Al_xGa_{1-x}N$ reststrahlen bands are not fully established and are replaced by thin dispersion lines. We found that all ω_{TO} frequencies determined by the fitting procedure correspond, within a few cm^{-1}, to the frequencies of the two extrema that can be read directly from the experimental spectra. We have obtained a free-electron concentration of 4.1×10^{18} cm^{-3} for the sample with 12% Al and 2.7×10^{18} cm^{-3} for the sample with 38% Al. For layers with higher Al content the free-carrier contribution can be neglected.

The dependence of phonon frequencies and oscillator strengths on $Al_xGa_{1-x}N$ composition are shown in Figs. 2(a) and 2(b), respectively. In Fig. 2(b), we show that the oscillator strength of AlN- and GaN-like TO phonons are, with a good approximation, simply proportional to the corresponding Al and Ga mole fractions, respectively. In Fig. 2(a), we show that the corresponding frequencies vary smoothly with alloy composition. This confirms the two-mode behavior of phonons in $Al_xGa_{1-x}N$. Finally, from the linear extrapolation of the experimental values for the GaN- and AlN-like phonon modes ($\omega_{GaN}=557+66\cdot x[cm^{-1}]$, $\omega_{AlN}=643+21\cdot x[cm^{-1}]$) we deduce 622 ± 5 cm^{-1} for the impurity (local) mode of Ga in AlN and 643 ± 5 cm^{-1} for the impurity mode of Al in GaN.

We have also computed the LO frequencies of the two polar modes using TO mode frequencies and oscillator strengths shown as solid lines in Figs. 2(a) and 2(b). These values are obtained as the peak positions of $\mathrm{Im}[\epsilon^{-1}(\omega)]$ and have been indicated as dashed lines in Fig. 2(a). The interesting point to stress is that these results agree well with the frequency of the sharp dip resolved on top of the SiC reststrahlen band, which was associated with an E_1(LO) mode. The composition dependence of its frequency is in good overall agreement with the composition dependence of LO phonons found in Raman experiments.[2,3]

Finally, the lower LO phonon branch, also indicated as a dashed line in Fig. 2(a), is not resolved either in this work or in Raman experiments reported up to now.[1–3] We have found that in the whole investigated alloy composition range the maximum in $\mathrm{Im}[\epsilon^{-1}(\omega)]$, corresponding to the low-frequency branch of LO mode, is at least an order of magnitude weaker than the maximum corresponding to the high-frequency one. This might be the reason why the low-frequency branch of the LO mode was not resolved up to now and might explain most of the previous experimental reports of a one-mode behavior for LO modes in $Al_xGa_{1-x}N$.

To conclude, measuring infrared reflectivity spectra of $Al_xGa_{1-x}N$ in a large composition range, we have demonstrated a two-mode behavior for the E_1(TO) phonon modes. This is in agreement with the theoretical predictions of Grille and Bechstedt,[16] but disagrees with most previous experimental reports. Finally, we have obtained a value of 622 ±5 cm^{-1} for the impurity mode of Ga in AlN and 643 ±5 cm^{-1} for the impurity mode of Al in GaN.

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