

Raman study of resonance effects in Ga_{1-x}Al_xN solid solutions

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The photoluminescence and Raman spectra of several Ga_{1-x}Al_xN layers ($0 \leq x \leq 0.86$) grown on sapphire substrates by metal-organic vapor phase epitaxy have been recorded at room temperature, under an excitation at 244 nm. Using the photoluminescence spectra, the variation of the band gap of these alloys can be followed only up to $x = 0.5$. From resonant Raman scattering, it can be deduced that the band gap energy of the solid solution for x very close to 0.7 corresponds to the incident photon energy (5.08 eV). This result is confirmed by a detailed comparison of the present work with previous experimental data on the A₁(LO) phonon peak position, obtained under visible excitation.

1 Introduction

Gallium aluminum nitride alloys are particularly suited to the technology of opto-electronic devices, particularly ultraviolet light emitters. Indeed, the width of their forbidden band can be tuned for many applications in this spectral range by varying the alloy composition. The basic physical properties of these solid solutions have been investigated only recently; concerning the dynamical properties of Ga_{1-x}Al_xN, they have been studied by Raman spectroscopy under excitation in the visible range [1] [2] [3].

The present measurements have been performed in view of studying the band gap in the Ga_{1-x}Al_xN alloys through resonant Raman scattering. Due to the strong electron-phonon Fröhlich interaction in polar crystals, a drastic enhancement of light scattering by polar LO phonons can be achieved in resonant conditions, i.e. when the energy of the incident (or scattered) photon is close to the band gap energy of the semiconductor. Generally, the resonant effect is evidenced on a given sample by varying the excitation energy. In the present work, this energy was kept constant and the intensity of the polar LO phonon was measured on several Ga_{1-x}Al_xN layers, thus varying the band gap energy with x .

It should be noted that the LO phonon observable in backscattering geometry along the c -axis of the wurtzite structure corresponds to the symmetry A₁; according

to the selection rules, it is allowed only when the polarizations of the incident and scattered light are parallel. So, far from resonance, the contributions of the allowed and “forbidden” (resonant) scattering processes cannot be distinguished, while the latter predominates only in resonant conditions.

2 Samples and experiments

We present photoluminescence and Raman measurements on a series of alloy samples with the wurtzite structure, covering a wide compositional range ($0 \leq x \leq 0.86$). The layers used for this study were grown at 980°C on sapphire substrates by organometallic vapor phase epitaxy, after the deposition of a thin AlN buffer layer [4]. Their thickness was typically 2 μm.

The excitation was achieved with the 244 nm line of a frequency doubled Ar⁺ laser. The corresponding energy ($E_L = 5.08$ eV) lies between the fundamental direct gap energies of GaN (3.4 eV) and of AlN (6.2 eV), at room temperature. The experimental setup was a Renishaw micro-Raman spectrometer, equipped with a diffraction grating with a 3600 m⁻¹ groove density; its spectral resolution was typically 7 cm⁻¹. The continuous extended (CE) scanning technique, developed by Renishaw, allows one to obtain data collection over the full spectral range of the spectrometer, particularly adapted for luminescence measurements far from the excitation

line. In the present experiments, the diameter of the laser spot on the samples was around 1 μm and the incident light power was lower than 1 mW.

3 Experimental results

First, the room temperature photoluminescence (PL) spectra of the $\text{Ga}_{1-x}\text{Al}_x\text{N}$ layers are displayed in Figure 1. The energy of the PL features is plotted versus the aluminum molar ratio x and compared with the band gap measured by Brunner et al. [5] in Figure 2. The near band edge luminescence can be observed in the spectra of gallium rich layers only. On the other hand, the intense PL structure found in the spectra for $x > 0.5$ does not follow the increasing band gap. This gives evidence for the increasing ionization energy of the centers involved in the recombinations; as suggested by Perry et al. [6], it may be essentially due to the spatial localization of the donor. The oxygen atoms, which are probably responsible for unintentional n type doping and, according to the work of Van de Walle [7], undergo a transition from shallow to deep centers in wurtzite $\text{Ga}_{1-x}\text{Al}_x\text{N}$ near $x = 0.5$, would be good candidates for the active donors in the solid solutions.

The Raman spectra, recorded at room temperature in the $z(x'x')\bar{z}$ configuration for six samples regularly spaced in the compositional range, are presented in Figure 3. They are quite different from the spectra obtained using visible excitation [3]. Under ultraviolet excitation, the non-polar (allowed) E_2 phonons are not in evidence, while multiphonon Raman scattering by the polar $A_1(\text{LO})$ phonon is observed up to fourth order. The resonance enhancement is maximum for $x = 0.72$. However, a significant increase in intensity is already observed for $x = 0.35$, although the difference between the corresponding fundamental band gap E_g and the laser energy E_L is as high as 1 eV in this case. Large resonance effects are responsible for this behavior, which was recently observed in pure GaN with wurtzite structure [8]. Indeed, the coupling constant characteristic of the Fröhlich interaction responsible for the enhancement of the polar phonon lines is six times as big in GaN as in GaAs [9].

The inset of Figure 3 shows the Raman spectra of the $x = 0.72$ layer recorded at three different temperatures. When decreasing the temperature, thus increasing the forbidden energy band of the sample, we observe a continuous enhancement of the $A_1(\text{LO})$ phonon line, suggesting that the band gap energy of this solid solution would be close to but still lower than $E_L = 5.08$ eV, at low temperature. Our results can be compared with recent absorption measurements [5] [10] on $\text{Ga}_{1-x}\text{Al}_x\text{N}$, at various temperatures. Using the phenomenological

dependence of the conventional band gap energy at room temperature, defined in ref. [10] and expressed (in electron volts) as:

$$E_g(x) = 3.45(1-x) + 6.13x - 1.3x(1-x) \quad (1)$$

we find for $x = 0.72$, $E_g = 5.11$ eV, which is close to the incident photon energy in our experiment $E_L = 5.08$ eV. The value of E_g would be still greater at liquid nitrogen temperature. However, no conclusion can be drawn from this little discrepancy, because the precision in the band gap determination is probably not sufficient, either from absorption measurements, or from experiments of resonant Raman scattering.

In Figure 4, the variation of the intensity of the $A_1(\text{LO})$ phonon is given as a function of the detuning dimensionless parameter $(E_g - E_L)/\hbar\omega_{\text{LO}}$. The values of E_g are taken from ref. [10]. Note the asymmetric shape of this resonance profile, around the maximum obtained experimentally for an aluminum molar ratio x close to 0.72.

In Figure 5, the frequencies of the $A_1(\text{LO})$ phonon measured under ultraviolet excitation are plotted versus the aluminum content x . They are compared with the previous results of a Raman study we performed under visible excitation [3] on the same samples (dotted line). A shift of the phonon line position between these spectra is in evidence for $x > 0.3$ and clearly changes sign around $x = 0.7$.

4 Modeling

The dependence of the peak position on the wavelength of the laser line can be explained in terms of local compositional inhomogeneity of the solid solutions [11]. In resonant conditions, the volume of the Raman probe for the Fröhlich type scattering processes corresponds typically to the polaron size. The polaron radius a_p can be calculated as [12]:

$$a_p = \frac{\hbar}{\sqrt{2m_p\hbar\omega_{\text{LO}}}}$$

Using for the phonon energy $\hbar\omega_{\text{LO}} = 92$ meV and taking for the polaron mass m_p a value close to the electron mass $m^* = 0.2 m_0$, as in GaN wurtzite crystal, we would find $a_p = 1.5$ nm, which is lower than the corresponding value in “usual” zincblende III-V semiconductors. Within the polaron volume V_p , the alloy composition can be significantly different from the nominal value. Because of statistical composition fluctuations, the LO phonon may be shifted from its off-

resonance value when a selective enhancement of the signal coming from locally GaN- or AlN-rich regions may be achieved through electron-phonon Fröhlich interaction.

In the following, x_0 corresponds to the (nominal) average value of the aluminum molar fraction in a given sample. The probability of finding the fraction x of aluminum atoms inside the (spherical) volume V_P of the polaron can be approximated by a distribution centered on the nominal composition x_0 with the following form:

$$\rho(x) = \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right]$$

using for the gaussian function the standard deviation deduced from a binomial distribution of cations .

$$\sigma^2 = \frac{x(1-x)}{nV_P}$$

Here, n stands for the cation volume density in the alloy. In resonant conditions, the most probable frequency of the LO phonon in the layer is given by the statistical average function [11]:

$$\omega(x_0) = \frac{\int dx \frac{\rho(x)}{[(E_L - E_g(x))^2 + \Gamma^2/4]^2} \omega_{LO}^v(x)}{\int dx \frac{\rho(x)}{[(E_L - E_g(x))^2 + \Gamma^2/4]^2}} \quad (2)$$

where $\omega_{LO}^v(x)$ is the phonon frequency determined far from resonant conditions, which may be expressed (in cm^{-1} units) from our previous results as [3] :

$$\omega_{LO}^v(x) = -51.8 x^2 + 199.7 x + 742$$

$E_g(x)$ is given by equation (1) and Γ is an parameter which is of the order of one phonon energy (the values $\Gamma = 60$ meV and $a_P = 1.3$ nm (instead of 1.5 nm, which was determined for pure GaN) have been chosen as best parameters for the calculation.

The solid line of Figure 5 is the plot of the frequencies $\omega(x_0)$ deduced from equation (2). A satisfactory agreement is found between the calculated values and the frequencies measured under ultraviolet excitation.

Obviously, the shift of the calculated LO phonon frequency with respect to the values of ref. [3] is vanishing when the nominal aluminum molar ratio is x_0 [ape] 0.7, i.e. when the condition $E_g(x_0)$ [ape] E_L is verified.

5 Summary

The band gap of $\text{Ga}_{1-x}\text{Al}_x\text{N}$ layers have been investigated using resonant Raman scattering under an excitation at $E_L = 5.08$ eV. The intensity variation of the longitudinal optic phonon shows that the band gap energy is close to E_L when $x = 0.72$. Moreover the frequencies of the $A_1(\text{LO})$ phonon are significantly shifted from the values obtained under visible excitation. The modeling of this frequency shift in terms of compositional fluctuations of the layers confirms that the band gap energy is close to E_L for a solid solution with an aluminum molar ratio $x = 0.7$, as it is found in the resonance profile.

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FIGURES

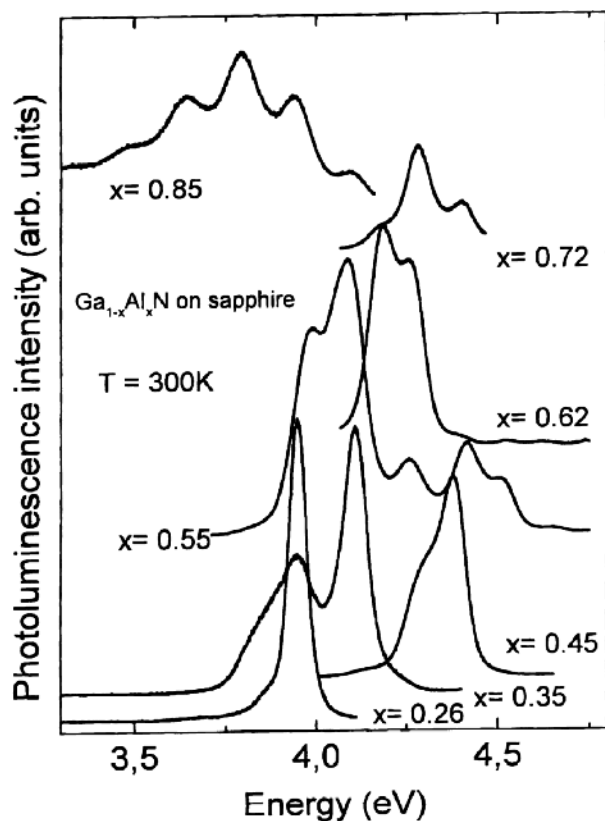


Figure 1. Photoluminescence spectra of the $\text{Ga}_{1-x}\text{Al}_x\text{N}$ layers recorded at room temperature

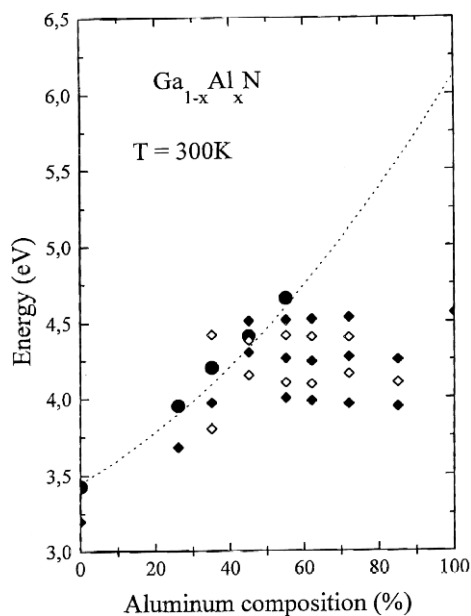


Figure 2. Energy of the experimental PL features versus the aluminum molar ratio x . The full circles correspond to near band edge luminescence and diamonds to other PL features. The alloy band edge from Ref. [5] is plotted in dotted line.

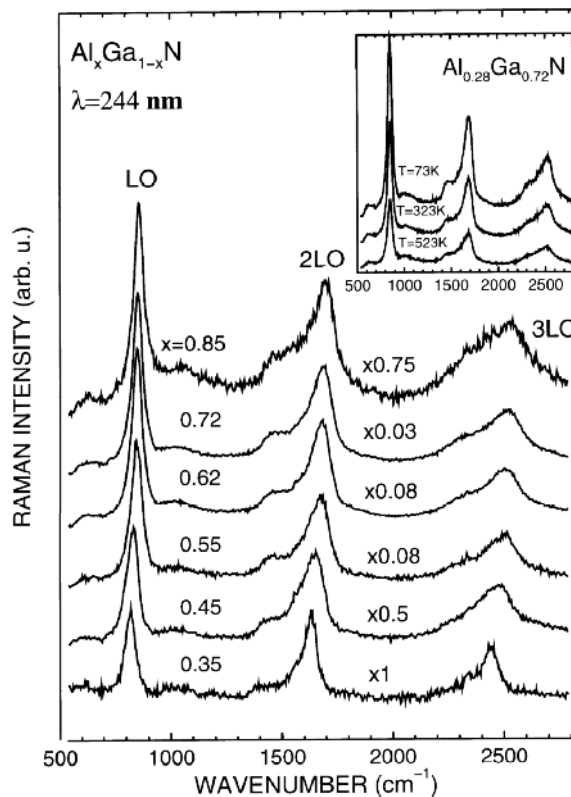


Figure 3. Raman spectra of the $\text{Ga}_{1-x}\text{Al}_x\text{N}$ layers recorded at room temperature in the $z(x'x')\bar{z}$ configuration. Insert: Raman spectra of the $\text{Ga}_{0.28}\text{Al}_{0.72}\text{N}$ layer recorded in the same configuration at three temperatures.

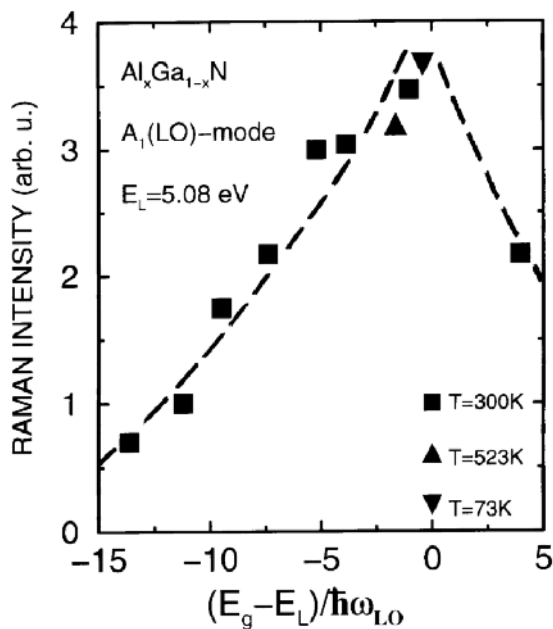


Figure 4. Resonance profile of the $A_1(\text{LO})$ phonon versus detuning $(E_g - E_L)/\hbar\omega_{\text{LO}}$ (see text). The dotted line is only a guide for the eye.

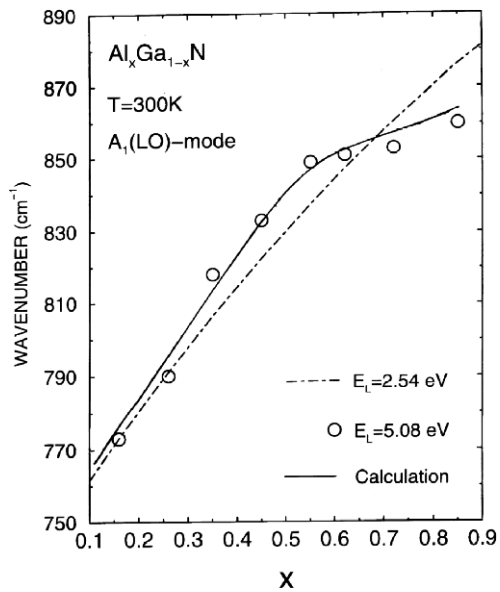


Figure 5. Plot of the calculated frequencies (solid line) and of the frequencies measured ultraviolet excitation (open circles), for the $A_1(LO)$ phonon. For comparison, the dotted line gives the variation of the frequencies measured under visible excitation.