Resonant Raman scattering in strained and relaxed InGaN GaN multi-quantum wells

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The effects of the composition and strain in InGaN/GaN multi-quantum wells on their phonon frequencies have been determined using resonant Raman scattering in a wide energy range. In pseudomorphic quantum wells a strong compensation of both effects occurs, resulting in the InGaN A_1LO phonon frequency being almost independent on In concentration. In relaxed quantum wells the A_1LO frequency is clearly below the GaN value and depends on the excitation energy, as reported in thick films. This variation, together with the resonance profile, gives a direct estimate of the In concentration and its fluctuations. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1861496]

The use of InGaN alloy layers in light emitting devices in the visible and UV ranges[1] has experienced an important growth in recent years. The use of spectroscopic methods to study material parameters, which are crucial to determine their optical properties is also increasing. In particular, photoluminescence (PL) emission has been widely used to determine the In concentration and its homogeneity, as well as the elastic strain and the corresponding piezoelectric field of InGaN layers.[2] Additionally, in quantum well (QW) systems the fluctuations in the well width and the possibility of In segregation[3] have also been studied by optical methods. Among them, Raman spectroscopy has proven to be a powerful method to investigate the properties of InGaN layers. Raman spectroscopy has been used in thick films[4–7] and in QW systems.[8–10] If the Raman excitation is brought in resonance with the electronic transitions of the QW the enhanced scattering cross section allows to measure only few nanometers thick InGaN layers.[9] In inhomogeneous systems, resonant Raman scattering (RRS) has a maximum intensity at the *average* value of the energy gap. It therefore gives information on the average properties of the sample. This is in contrast to PL measurements, which, due to the efficient carrier relaxation, only involve the *lowest* transition energy,[5] corresponding to sample areas with extreme values of composition, strain, or piezoelectric field. RRS measurements in InGaN layers are scarce[5,8,9] due in part to the relatively uncommon use of tunable lasers for excitation in the blue-green spectral region. Sometimes this difficulty is overcome by varying the sample temperature to sweep through the resonant condition. This method has been used to record RRS profiles in InGaN QW.[8] The drawback of this method is that the temperature variation can strongly affect the strain, due to the difference in thermal expansion coefficients between the substrate and the rest of the sample or between GaN and InGaN. Consequently, the phonon frequency and the resonance energy itself are changed during the measurement.

In this letter we report RRS measurements in the excitation energy range between 2.0 and 3.0 eV at constant temperature in InGaN/GaN multiquantum wells (MQWs) for both pseudomorphic and relaxed samples. In the former we find an almost complete cancellation of the A_1LO frequency decrease from GaN to InGaN due to the In incorporation with the frequency increase due to the biaxial compression, as in the case of strained thicker layers.[7] The relaxed sample has a lower A_1LO frequency, which depends on the excitation energy due to selective resonant enhancement. This variation, together with the resonance energy, allows the determination of the In concentration and its fluctuation range.

The samples studied are formed by five QWs of InGaN with nominal In concentration around 15% separated by GaN barriers. They have been grown by molecular beam epitaxy (MBE) on a (0001) 300 nm thick GaN template deposited on a sapphire substrate.[11] The growth temperature of the wells and the barriers was the same (570 °C), to avoid In desorption during the process. A GaN cap layer of 6 nm has been grown on top of the structure. The nominal dimensions and In content of the two samples studied (A and B) are shown in Table I. The barrier and well widths (d_B and d_w, respectively) have been estimated from x-ray diffraction and high resolution transmission electron microscopy (HRTEM). Asymmetric x-ray diffraction measurements performed in our samples indicate qualitatively that lattice relaxation in sample A is much stronger than in sample B. The RRS experiments were performed at room temperature using rhodamine 110 and stilbene 3 (UV pumped) dye lasers and an Ar-ion laser to cover the 2.0–3.0 eV spectral range. The typical excitation power was 30 mW. The scattered light was

TABLE I. Thickness of the quantum wells (d_w) and barriers (d_B) and In concentration (x) determined by XRD and HRTEM analysis.

Sample	d_w(nm)	d_B(nm)	x
A	5.0	6.0	0.16
B	2.5	5.5	0.14
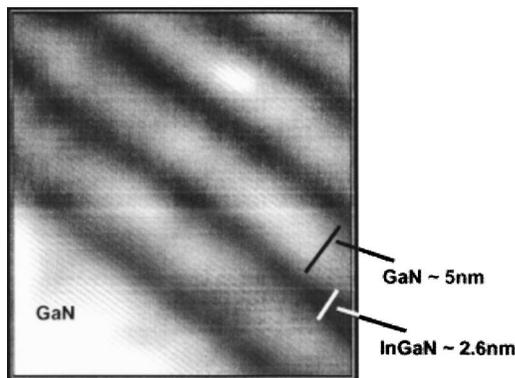
FIG. 1. HRTEM image (after Fourier filtering) of sample B showing the InGaN quantum wells.

FIG. 3. Frequency of the A_1LO phonon of InGaN of sample A vs excitation energy.

dispersed by a double spectrometer and a cooled silicon CCD detector.

The *cross-sectional* HRTEM image of sample B, is shown in Fig. 1. The QWs are clearly visible with contrast variations which are indicative of inhomogeneous In concentration or width fluctuations in the QW layers. The Raman spectra of the two samples are shown in Fig. 2 for different excitation energies. The spectra are normalized to the intensity of the E_2 phonon of GaN at 568 cm^{-1}. Sample A [Fig. 2(a)] displays three peaks in the high frequency side corresponding to the sapphire substrate at 750 cm^{-1} (marked with an arrow), the A_1LO mode of GaN at 735 cm^{-1} (vertical dashed line) and the A_1LO mode of InGaN around 710 cm^{-1}. The E_2 phonon of InGaN is not detected, because its nonpolar character strongly reduces its resonant enhancement when compared to the LO modes. The A_1LO mode of InGaN is considerably broader than the GaN one and its frequency increases with increasing excitation energy. This is a direct consequence of the selective excitation of RRS in sample regions with different In content, as observed in InGaN thick films.[5,8] The spectra of sample B [Fig. 2(b)] excited at high energy show a strong band around 730 cm^{-1} corresponding to the A_1LO mode of InGaN. Its large intensity in spite of the small scattering thickness (12.5 nm) indicates an extremely efficient resonant enhancement. In this case the phonon frequency is only 3–5 cm^{-1} below the GaN value. The expected frequency shift of the A_1LO phonon for relaxed

InGaN with In concentration x is $\Delta\omega_x = -149x$,[7] while for biaxial strain the shift is given by:

$$\Delta\omega_S = 2\left(a_\lambda - \frac{C_{13}}{C_{33}}b_\lambda\right)\frac{a_{GaN} - a_{InN}}{a_{InN}}x. \tag{1}$$

Using the values of the elastic constants C_{13} and C_{33} and the in-plane lattice parameters $a_{(Ga,In)N}$, given in Ref. 12, interpolated for $x=0.15$, and the phonon deformation potentials $a_\lambda = -850$ cm^{-1} and $b_\lambda = -920$ cm^{-1} (Ref. 13) one obtains $\Delta\omega_S = 119x$. For $x=0.15$ the total expected shift for pseudomorphic QW is $\Delta\omega = \Delta\omega_x - \Delta\omega_S = -4.5$ cm^{-1}. This value is in agreement with the result of Fig. 2(b), where such a small shift cannot be detected because the signal is too weak for excitation below 2.7 eV. The frequency shift for relaxed QW amounts $\Delta\omega_X = -22$ cm^{-1}, coinciding with the average value shown in Fig. 2(a). One can then conclude that sample A is essentially relaxed, while sample B is fully strained, in
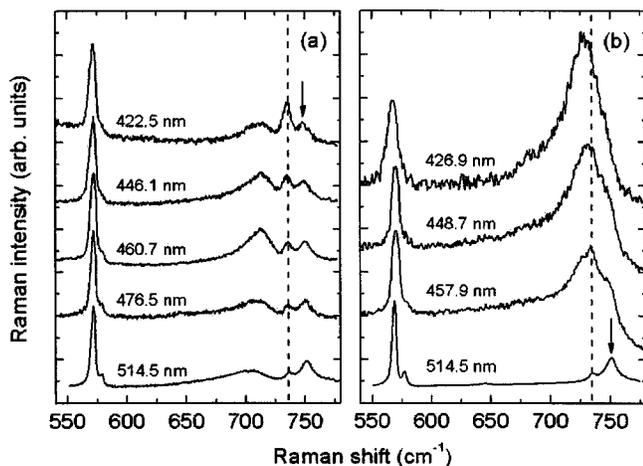

FIG. 2. Raman spectra for different excitation wavelengths for (a) samples A and (b) B, respectively. The arrows show the E_2 phonon of the sapphire substrate. The vertical dashed line coincides with the A_1LO phonon of GaN.
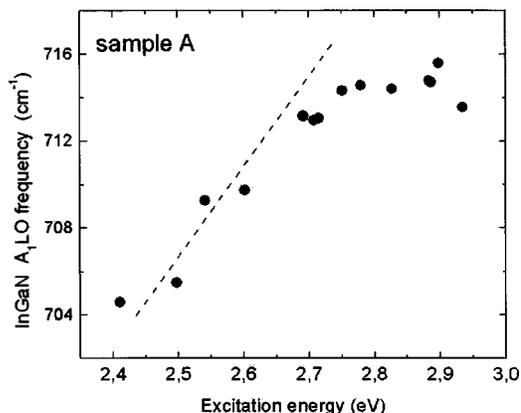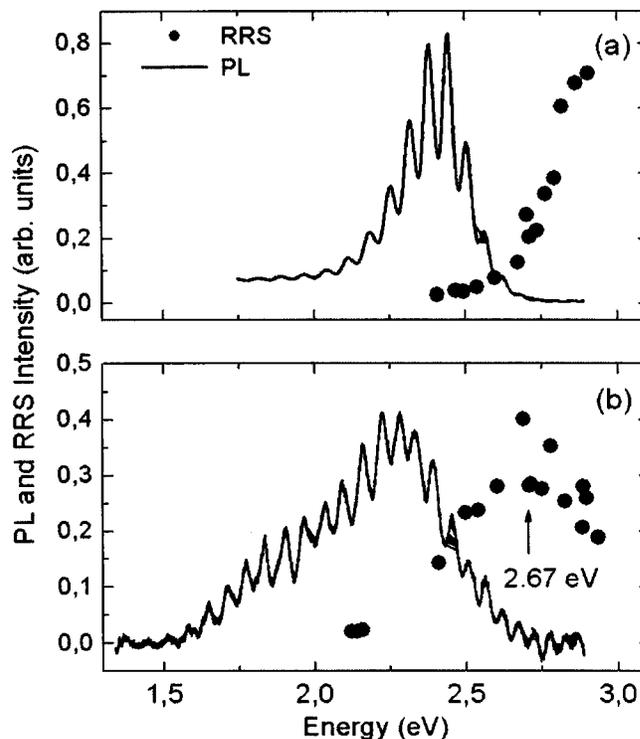

FIG. 4. PL emission spectra (solid lines) and RRS profiles (dots) of the (a) samples A and (b) B.

agreement with the asymmetric x-ray scattering results. The critical thickness for relaxation of InGaN layers with x $=0.16$ is expected to be around $d_w=40$ nm,[14] a much larger value than the well thickness of sample A. The origin of the relaxation in sample A is probably due to our specific growth conditions (constant low temperature and Ga flux), which are not optimal for GaN growth. This might induce some degree of three-dimensional growth in the barriers resulting in a strain relaxation as the layer width is increased.

The frequency change of the A_1LO phonon in sample A is shown in Fig. 3 as a function of excitation energy. Its decrease for decreasing energy is indicative of inhomogeneous In distribution. Comparing the data in Fig. 3 with the results of Ref. 7, one obtains In concentrations ranging from $x=0.14(715$ cm$^{-1})$ to $x=0.21(704$ cm$^{-1})$. These values compare well with the average one determined by x-ray diffraction shown in Table I. Moreover, if one compares the expected change in the band-gap energy with $x(dE_G/dx)$ for $x<0.2$:

$$\frac{dE_G}{dx} = E_{\text{InN}} - E_{\text{GaN}} - b + 2bx, \qquad (2)$$

where $b=3.4$ eV (Ref. 15) is the bowing parameter, and the phonon frequency change given above,[7] $\Delta\omega_x=-149x$ cm^{-1}, one obtains that the phonon frequency for $x=0.17$ should vary with the resonant excitation energy as

$$\frac{d\omega}{dE_G} = -\frac{149}{|dE_G/dx|_{0.17}} = 40 \text{ cm}^{-1}/\text{eV}. \qquad (3)$$

This is the slope of the dashed line in Fig. 3, which fairly reflects the experimental behavior below 2.7 eV. Above this energy the phonon frequency does not change appreciably. A possible explanation could be that the In concentration distribution is not continuously decreasing. Instead it seems to have a lower limit (0.14) corresponding to the saturation of the phonon frequency around 715 cm^{-1}.

The RRS profiles (the A_1LO phonon intensity versus excitation energy) of samples A and B are shown in Figs. 4(a) and 4(b), respectively, together with their PL emission spectra. The blueshift of the RRS with respect to the PL was already observed in thick films.[5] It is another consequence of the inhomogeneity of the In concentration. The lower PL emission energy of sample A is consistent with its lack of strain and the wider QW. The maximum of the RRS profile is observed in sample A at 2.67 eV. According to Eq. (2) (integrated in x) this corresponds to $x=0.17$, in excellent agreement with the average value obtained from the phonon frequency. For sample B only the low energy side of the RRS profile was accessible to our excitation energy range.

In conclusion, we report RRS measurements on both pseudomorphic and relaxed InGaN/GaN QW, which reveal important differences. In the pseudomorphic QW, a strong compensation of composition and strain effects makes the frequency of the A_1LO phonon almost independent on In concentration. In relaxed QW, the phonon frequency and intensity dependencies on excitation energy give accurate information on the In concentration and on the homogeneity of its distribution.

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