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Raman spectroscopy of GaAs and InGaAs under pressure

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Abstract. Strained layers of InGaAs on GaAs have been studied by Raman scattering under high pressure. More accurate values are given for the frequencies of the LO and TO phonons in GaAs and their pressure dependence. The frequency and pressure dependence of the LO GaAs-like phonon in 20% InGaAs is also reported. It is shown that the Raman shift at the phase transition at high pressure is a valuable diagnostic, allowing comparisons of different experiments. The phase transition pressure of the ternary alloy is consistent with linear interpolation between the binary compound values.

1. Introduction

The structural and elastic properties of semiconductor layers under large strains are important for a full understanding of the pseudomorphic strained layers now routinely incorporated in semiconductor devices such as lasers. There is considerable uncertainty about non-linear effects which are not negligible at strains of the order of 1% to 2%. Biaxial misfit strain includes a large hydrostatic component, and the interaction between the hydrostatic and the shear strain components in the non-linear regime is not well understood. For a review, see Dunstan (1997).

Measurements of the Raman spectra of pseudomorphic and relaxed layers under high pressure may be expected to provide useful data, since the Raman shift with pressure is directly linked with the non-linear interatomic force constant. This paper reports a preliminary study of a variety of InGaAs layers grown on GaAs. We obtain improved data for the Raman of GaAs at ambient pressure and under pressure. Some data is obtained for the InGaAs, and the results suggest what further samples may be necessary in future studies.

2. Experimental details

2.1. Samples and techniques

Four samples were studied. All were layers of InGaAs grown on GaAs by molecular beam epitaxy (MBE) and are detailed in table 1. Two samples were grown at RSRE (DRA Malvern) on (001) GaAs by conventional MBE (ME821 and ME535). They have been previously studied by high-resolution x-ray diffraction (HRXD) (Dunstan *et al* 1991a). One sample was grown at UPM Madrid on (111) GaAs by conventional MBE (No 269B) and was studied by HRXD and Raman scattering (Calle *et al* 1995). The final sample was grown at CNM Madrid by atomic layer MBE (G3178-1).

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Table 1. Sample details and data obtained from them.

	ME535	ME821	G3178-1	No 269B
Orientation	001	001	001	111
Thickness d (nm)	3000	70	100	87.5
Composition x	0.20	0.20	0.49	0.22
Strain ε	0.0016	0.012	0.0060	0.014
GaAs P_t (kbar)	172	(148)[a]	—	172
GaAs $\omega_{0,LO}$ (cm^{-1})	291.3	291.4	291.8	290.5
GaAs Ψ_{LO} (cm^{-1})	875	909	907	900
GaAs $\Delta\omega_{LO}(P_t)$ (cm^{-1})	49	50	—	51
GaAs $\omega_{0,TO}$ (cm^{-1})	267.6	267.5	267.6	267.6
GaAs Ψ_{TO} (cm^{-1})	956	—	—	982
GaAs $\Delta\omega_{TO}(P_t)$ (cm^{-1})	52	55	—	55
InGaAs P_t (kbar)	141	—	120	—
InGaAs $\Delta\omega_{LO}(P_t)$ (cm^{-1})	41	—	—	—
InGaAs $\omega_{0,LO}$ (cm^{-1})	285.8	—	—	—
InGaAs Ψ_{LO} (cm^{-1})	925	—	—	—

[a] Untrustworthy value—see text

Samples were thinned to about 30 μm thick by polishing most of the substrate away with fine diamond polishing paper, and then cleaved to about 50 μm $\times$ 100 μm for loading in the diamond anvil cell. Argon was used as the pressure medium and a small piece of ruby was included to serve as the pressure calibrant. Measurements were made at room temperature. The cell was placed under the microscope of a Renishaw Raman system, and a few mW of 632.8 nm He–Ne laser light focused onto the sample or the ruby. Back-scattered Raman light or ruby fluorescence was collected by the same microscope and analysed by the Renishaw spectrograph and CCD camera. Pressure changes were made *in situ*.

Only in the case of the thick relaxed 3 μm layer of 20% InGaAs could the Raman peaks we observed be attributed unambiguously to the InGaAs. In the thin strained layers the InGaAs Raman peak is expected to be weak, and within 2–3 cm^{-1} of the GaAs Raman peak, and we believe that in these cases it is the GaAs substrate peaks that we observe.

Raman signals from a semiconductor are expected to be weak when the band-gap is less than the energy of the laser and to increase dramatically when the band-gap is resonant. Also at resonance, selection rules break down and the 2LO peak becomes much more intense. Above resonance, when the sample is transparent to the laser light, the Raman signals generally remain intense because a greater volume of sample may contribute to the signal. In the 001 orientation, the TO phonon is forbidden in the back-scattering configuration we use here and is very weak below resonance. Above resonance it can generally be observed both because of the larger volume of crystal and by forward scattering with reflection from the rear of the sample. In our samples, from the known pressure dependence of the band gaps, resonance is expected with the 632 nm He–Ne laser radiation at about 50 kbar for the GaAs substrates, 70 kbar for 20% InGaAs and 100 kbar for 50% InGaAs.

We now consider the results from each sample in turn. The quantitative results are summarized in table 1.

2.2. Results

2.2.1. Thick relaxed layer ME535. Figure 1 shows the spectrum of the thick relaxed layer at a pressure where the InGaAs layer is transparent to the laser radiation and we expect to

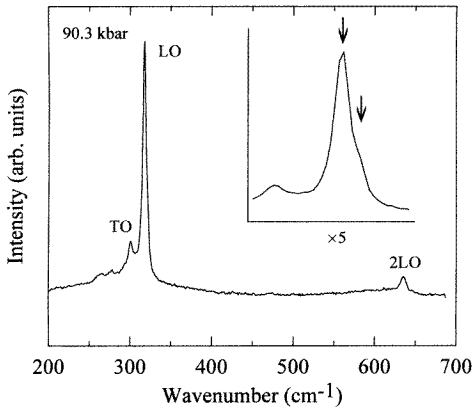

Figure 1. Raman spectrum of the thick relaxed layer of 20% InGaAs on 001 GaAs, ME533, recorded at 90 kbar, above resonance for the GaAs and at resonance for the InGaAs. The TO, LO and 2LO peaks are indicated. The LO is shown expanded in width ×5 in the inset. It clearly resolves into two peaks, whose positions are marked by arrows.

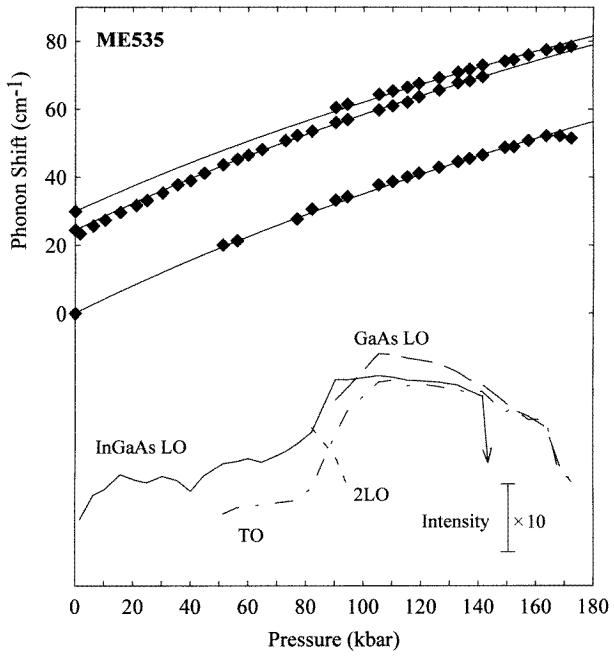

Figure 2. The pressure dependence of the peak positions and intensities observed in the thick relaxed layer of 20% InGaAs on 001 GaAs, ME533. The intensities are plotted logarithmically, and the scale bar shows a factor of ten. The solid lines are fits to a linear dependence of the Raman shift on density, using equation (1).

observe both the layer and substrate peaks. The two LO phonon peaks are indeed observed, but the TO phonon peaks, forbidden in this configuration, are too weak for two contributions to be resolved. Figure 2 shows the pressure dependence of these three peaks, together with their changes in intensity with pressure. The solid curves are least-squares fits to a linear

dependence on the density of the GaAs, obtained using the Murnaghan equation of state

$$\Delta\rho(P) = \rho(P) - \rho_0 = \rho_0\left(\left(1 + \frac{B'P}{B_0}\right)^{1/B'} - 1\right)$$
$$\omega(P) = \omega_0 + \tfrac{1}{3}\Psi\frac{\Delta\rho}{\rho_0} \qquad (1)$$

using the parameter values $B = 750$ bar and $B' = 4.5$ (Dunstan 1996). We use the coefficient $\frac{1}{3}\Psi$ for comparability with workers who use a fit to a lattice constant. At ambient pressure we observe only a single LO peak, at 285.8 cm^{-1}. This is in good agreement with Burns *et al* (1987) for the GaAs-like phonon in relaxed 20% InGaAs, giving a shift of the Raman peak with indium content of 6 cm^{-1}. For pressures up to about 80 kbar we see only this one LO phonon peak. At about 80 kbar, it increases strongly in intensity, corresponding to the InGaAs band-gap becoming resonant with the He–Ne laser radiation. Also at this pressure, first, the 2LO peak is briefly observed (as expected at resonance) and then a second LO peak at slightly higher wavenumbers, which we identify as the GaAs LO. Above resonance the InGaAs is transparent to the laser light and both the InGaAs and the GaAs substrate give a strong LO peak. At 141 kbar the InGaAs LO Raman signal disappears completely. This is interpreted as the phase transition of the InGaAs to a denser crystal structure. The GaAs LO peak continues above this pressure, although at reduced intensity. Presumably the high pressure phase of the InGaAs permits some excitation and Raman light to penetrate, although whether this is due to cracking and delamination of the InGaAs layer or to a low absorption coefficient is not clear.

The TO peak in this sample is not detectable at ambient pressure, but becomes apparent at 51.3 kbar, the pressure at which the GaAs becomes resonant with the laser. Its intensity then follows the same behaviour as the GaAs LO peak, rising at the InGaAs resonance and surviving until the GaAs phase transition. This peak may therefore be identified as the GaAs TO phonon.

2.2.2. Thin strained layer ME821. Figure 3 shows the pressure dependence of the Raman peak positions and their intensities in this sample. The pattern is very similar to figure 2, with the 2LO seen at resonance and the TO seen above resonance. However, resonance here occurs at 48 kbar, and so we attribute the LO, 2LO and TO phonons to the GaAs substrate. The ambient pressure peak positions are consistent with this interpretation, and the shifts with pressure are close to the values reported by Besson *et al* (1991). However, a comparison of the peak positions and the pressure at the GaAs phase transition, where the Raman peaks are lost, leads us to conclude that there was a significant error in pressure calibration in this run. This will be considered further in the discussion below.

2.2.3. 50% InGaAs layer G3178-1. Here again below resonance only the LO phonon could be observed at a position consistent with identification as the GaAs LO, and at 50 kbar (GaAs resonance) the LO became much more intense and the TO became detectable. However, both peaks became much weaker at about 90 kbar and undetectable above 115 kbar. This can be attributed to the InGaAs phase transition.

2.2.4. 111-oriented InGaAs layer No 269B. In the 111 orientation, the TO phonon is not forbidden in back-scattering and so dominates the Raman spectrum from ambient pressure. The increase in intensity of both the LO and TO at 45 kbar (figure 4) and the appearance of the 2LO peak at 45 kbar identifies them all as GaAs, and this is consistent with their quenching at the GaAs phase transition pressure, at 175 kbar.

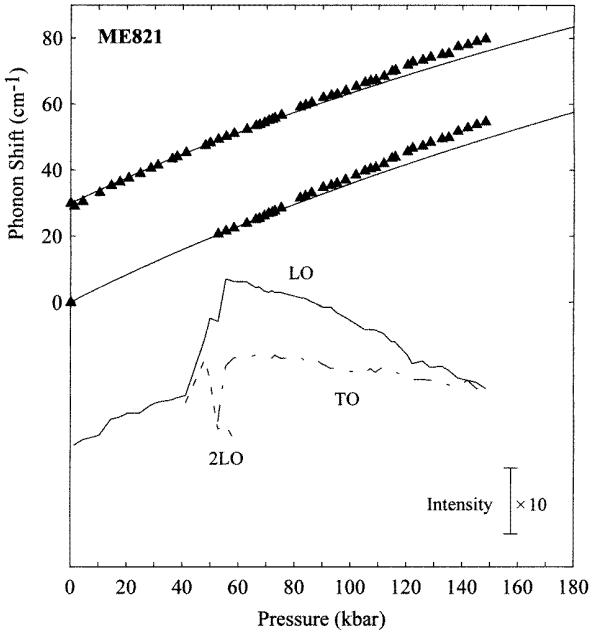

Figure 3. The pressure dependence of the peak positions and intensities observed in the thin strained layer of 20% InGaAs on 001 GaAs, ME821. The intensities are plotted logarithmically, and the scale bar shows a factor of ten. The solid lines are fits to a linear dependence of the Raman shift on density, using equation (1), and fitting to the data below 70 kbar only.

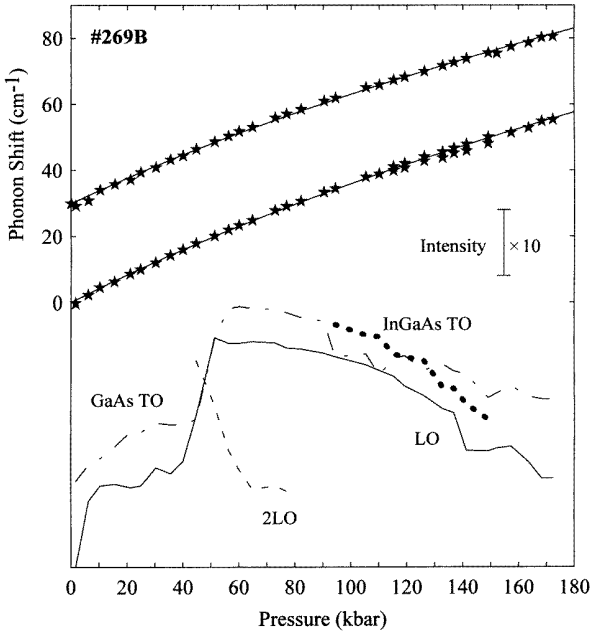

Figure 4. The pressure dependence of the peak positions and intensities observed in the thin strained layer of 20% InGaAs on 111 GaAs, No 269B. The intensities are plotted logarithmically, and the scale bar shows a factor of ten. The solid lines are fits to a linear dependence of the Raman shift on density, using equation (1).

From 115 kbar to 149 kbar, the TO phonon peak shows evidence of splitting, and we tentatively identify the lower energy peak as the InGaAs TO. If this attribution is correct, the InGaAs phase transition may be placed at 149 kbar.

3. Discussion

3.1. GaAs Raman parameters

Two of the samples (No 269B and ME535) gave clear-cut GaAs LO and TO phonon peaks at the GaAs phase transition pressure of 172 kbar and a Raman shift at this pressure of 49.5 ± 1 cm^{-1} (LO) and 55 ± 1 cm^{-1} (TO) from the ambient pressure positions. A least squares fit to these data and to ambient pressure data from all the samples gives

$$\omega_{LO} = 291.2 + (296 \pm 3)\frac{\Delta\rho}{\rho_0} \text{ cm}^{-1}$$

giving $\Psi_{LO} = 890 \pm 10$ cm^{-1}, and

$$\omega_{TO} = 267.6 + (323 \pm 3)\frac{\Delta\rho}{\rho_0} \text{ cm}^{-1}$$

giving $\Psi_{TO} = 970 \pm 10$ cm^{-1}, and the LO–TO splitting is

$$\omega_{LO} - \omega_{TO} = 23.6 - 27\frac{\Delta\rho}{\rho_0} \text{ cm}^{-1}$$

with P and ρ related through equation (1), as the best descriptions of the phonon energies at ambient pressure and under pressure. The ambient pressure values are in good agreement with other Raman determinations (Besson *et al* 1991, Trommer *et al* 1976). Data-book values are ω_0 of 285 cm^{-1} (LO) and 267 cm^{-1} (TO) (Madelung 1991) and the LO value should be corrected to the Raman value of 291–292 cm^{-1}. The pressure dependence is in good agreement with Trommer *et al* and significantly less than Besson's values.

The crucial feature of the behaviour of sample ME821 is that the maximum Raman shift was the same as in these two samples, 50 ± 1 cm^{-1} for the LO and 54 ± 2 cm^{-1} for the TO. This behaviour is consistent with a large error in pressure calibration. The data begins to diverge from the best fit at about 100 kbar. There are many things that can go wrong in a high-pressure experiment, some more explicable than others; the important point is to be able to detect a problem. The maximum shift of the Raman peak at the phase transition provides one such diagnostic. The data reported by Besson *et al* behave in the same way (maximum shifts of 51 cm^{-1} and 57 cm^{-1} for the LO and TO at 140 kbar), and we suggest were subject to a similar error.

3.2. InGaAs Raman parameters

Sample ME535 gave

$$\omega_{LO} = 285.8 + (308 \pm 3)\frac{\Delta\rho}{\rho_0} \text{ cm}^{-1}$$

giving $\Psi_{LO} = 925 \pm 10$ cm^{-1}, for 20% InGaAs with a small residual strain. None of the samples studied here gave an unequivocal result for the InGaAs TO phonon. Nor did they yield enough information to allow us to separate the dependence of the InGaAs Raman frequencies on indium content and on strain; nor to detect the dependence on the difference between the elastic constants of the layer and of the substrate. However, these experiments have shown what is required for further work: either samples several hundred nm thick, or tunable Raman rather than the fixed He–Ne wavelength we used, so that the InGaAs layers can be studied in resonance at a range of pressures.

3.3. Phase transition pressures

These data confirm the accepted phase transition pressure of GaAs at about 175 kbar. Besson *et al* (1992) give evidence that, rather than occurring at a single well defined pressure, the phase transition is spread over the range 120–220 kbar. The comparison we make here between their Raman measurements (reported in most detail in Besson *et al* (1991)) and ours suggests that 120 kbar is too low. A range of ± 10 or 20 kbar around 175 kbar, depending on the experimental technique and the pressure and temperature conditions, may be more plausible, and consistent with our recent analysis of data for InP (Whitaker and Dunstan 1998).

We have also observed the phase transition in relaxed 20% InGaAs (from the loss of its Raman signal, figure 2) and in strained 50% InGaAs (from the weakening of the GaAs Raman, figure 5). In figure 6 the results are plotted, not as the phase transition pressure but as the LO Raman frequency of the GaAs substrate at the phase transition against In content. This procedure avoids errors in pressure calibration and reconciles, as we have seen, the GaAs data. For our InGaAs samples, the plotted points are experimental values taken directly from figures 2 and 5. For the 50% sample, the point plotted is at 108 kbar, typical of the values seen after the drop in intensity from 100 kbar. For InAs, we have plotted the GaAs Raman shift from figure 2 at the phase transition pressure of InAs of 76 kbar reported by Aoki *et al* (1984). An uncertainty in the data of ± 2 cm^{-1} is consistent with the scatter of the GaAs data. The values for both the thick relaxed 20% layer and the thin strained 50% layer are consistent within experimental uncertainty with linear interpolation between the phase transition pressures of bulk GaAs and bulk InAs.

The phase transition pressure in quantum wells is known to be affected by the adjacent material (Weinstein *et al* 1987, Dunstan *et al* 1991b), but the mechanism is not sufficiently well understood to predict whether it should operate in the 50% layer which is 100 nm thick. The residual strain in the 20% layer is only 0.16% (table 1), implying stresses of about

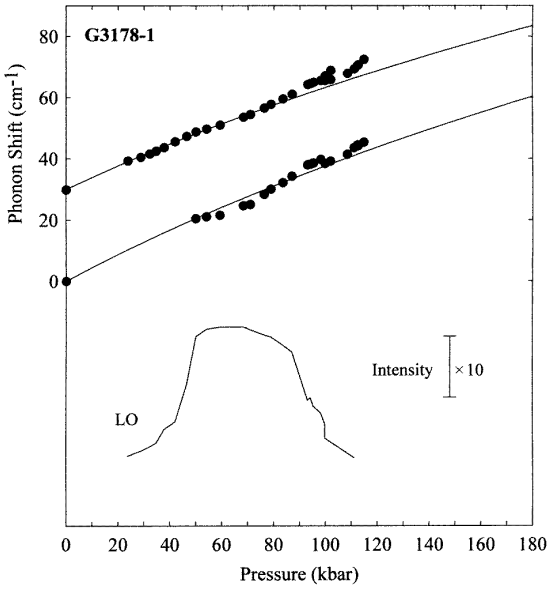

Figure 5. The pressure dependence of the peak positions and intensities observed in the thin strained layer of 50% InGaAs on 001 GaAs, G3178-1. The LO intensity is plotted logarithmically, and the scale bar shows a factor of ten. The solid lines are fits to a linear dependence of the Raman shift on density, using equation (1).

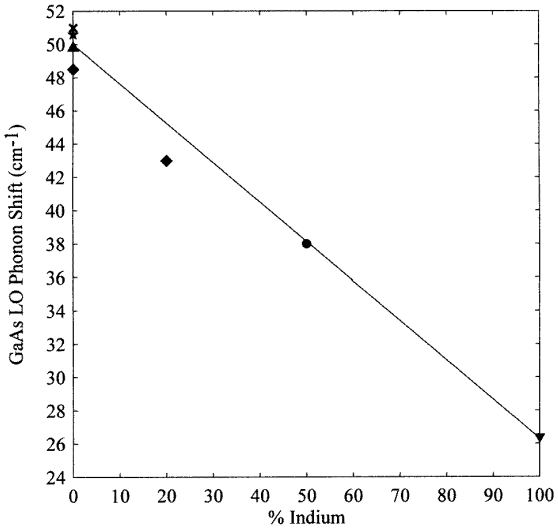

Figure 6. The GaAs LO Raman shifts at the phase transitions in our samples are plotted against indium content. Data from the literature are also shown for GaAs (the highest data point), from Besson *et al* (1991). For InAs (▼), we use the phase transition pressure of 76 kbar from Aoki *et al* (1984), and equation (1) with $\Psi_{LO} = 890\ \mathrm{cm}^{-1}$. The straight line is a guide to the eye. The scatter of the GaAs data suggests uncertainties of about $\pm 2\ \mathrm{cm}^{-1}$ on all data points.

2 kbar (biaxial) and 1 kbar (hydrostatic component). The strain of 0.6% (table 1) in the 50% layer corresponds to biaxial and hydrostatic compressive stresses of about 6 kbar and 4 kbar respectively. There are no theoretical predictions of the effect of such strains on the phase transition pressure; from our data they are less than the experimental uncertainty.

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