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LETTER TO THE EDITOR

Zone-edge phonons—a microprobe of strain at the interface of lattice mismatched epitaxial layers

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Abstract. We demonstrate the strength of second-order Raman scattering in probing strain limited to mesoscopic dimensions. This method is shown to be powerful in evaluating the degree of homogeneity at the interface of mismatched epitaxial layers. We use this method to re-examine neutron scattering results of the LO phonon frequencies at zone edge.

A detailed study of the properties of the lattice mismatched epilayers is essential for the understanding of the behaviour of quantum wells and superlattices based on these epilayers. There are a large variety of methods for characterizing such epitaxial layers, we shall restrict ourselves to Raman scattering and show that by this non-destructive method, fine details can be probed on a scale which is two orders of magnitude smaller than the laser wavelength.

The determination of strain within lattice mismatched epilayers via the LO phonon frequency shift became common practice because of the simplicity and convenience of the Raman technique. This is normally done using the back-scattering Raman arrangement and was actually also reported [1] for the system with which we deal here. We have proven [2] that when the layer thickness becomes larger than the critical one, a layer of lower strain (and of larger lattice parameter) is formed, preserving the higher strain of the former grown layer. It therefore means that for large light penetration depth the measured LO phonon line is composed of LO line frequencies contributed by scattering from different depths of the layer, which may be at different strains. This has been shown [3] to vary stepwise with thickness in the case of InGaAs/GaAs. The Raman scattering technique is also used to assess the strain depth-profile taking advantage of the feasibility in changing the laser wavelength and thereby the light penetration depth [1]. The light penetration depth is affected by the degree of disorder [4] on the one hand and the change in the electronic structure on the other, and these two are not independent. Except for special cases, the reported LO frequency shift was typically of the order of a couple of wavenumbers; such a minor shift was insufficient to resolve fine details in the strain depth-profile.

Apart from the question of the depth profile of the strain there is another crucial problem: is the strain homogeneous at a fixed depth and in particular, at the interface? Using a micro-Raman set-up, the spatial resolution is diffraction limited

to the laser wavelength. In addition to this limitation there is another basic aspect that should be considered in this context. Raman scattering has to obey momentum conservation, namely $k \sim 0$, which for first-order scattering involves only phonons with wavelengths of the order of the laser line. This means that features of size much smaller than that, belonging to the *same* vibrational mode, may be averaged and therefore washed out. This is *not* the case for Raman scattering of two-phonon combinations, summation or difference bands, where the main contribution comes from zone-boundary (ZB) phonons, because of their higher density of states (for this case harmonics of zone-centre phonons are excluded). In this case $k \sim \pi/a$, which corresponds to a wavelength of the order of 10 Å; the actual symmetry point is insignificant. We have already shown this [2] by means of TO–TA phonon frequency shift and have proposed *that the effect is general, for any zone-edge phonon.* In this letter we prove that this is really the case and that the method is impressively powerful.

The samples investigated in the present study were grown by both metal organic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE). The method of growth did not have any effect on the experimental results reported here. The ZnSe layers grown by MOVPE at 325° C were 3.6 μm and 0.1 μm thick and that grown by MBE at 320° C was 2.5 μm thick, each on the (100) face of GaAs. The critical thickness of ZnSe/GaAs was determined [5] to be in the range of 1500 Å by x-ray diffraction and transmission electron microscopy as well as from Raman scattering [1]. Therefore the thickness of two of the epilayers is *considerably larger than the* critical thickness, the 0.1 μm thick sample is obviously smaller.

The Raman measurements were taken with the Ar^+ 5145 Å line, *not* at resonance with the ZnSe layer. Two configurations were used: (i) the conventional one of nearly back-scattering from the thinnest sample (below the critical thickness), in the $\bar{z}(x'x')z$ configuration, for which only scattering by LO phonons is allowed; (ii) probing the scattering from a cleaved plane perpendicular to the interface, in the $\bar{z}'(x'x')z'$ configuration (z' and x' refer to $[1\bar{1}0]$ and $[110]$ directions respectively); in this configuration only scattering by TO phonons is allowed. The Dilor multichannel triple monochromator was used at room temperature with the microscope option at a magnification of $\times 100$. The laser beam waist at the sample amounted to approximately 500 nm, while the laser power was kept sufficiently low to prevent heating.

We shall concentrate mainly on the results obtained by using the second configuration (ii), where the region at the interface is directly probed. The proximity of the examined site of ZnSe to the interface is viewed by the intensity ratio of the TO lines of GaAs and ZnSe. This turns out to be an extremely sensitive criterion, though has not been used to quantify the distance from the interface. It has already been shown [2] that while the TO line frequency hardly shifts, which is in agreement with earlier uniaxial stress measurements, the TO–TA line shows a maximal shift of 18 cm^{-1}. We interpreted [2] this huge frequency shift as due to local high strain, which remains unnoticed when probed by first-order Raman scattering due to the relatively large wavelength corresponding to $k \sim 0$. TO–TA combines zone-boundary phonons with an extremely short wavelength and is therefore capable of probing mesoscopic-size islands of high strain. This being a general property of zone-edge phonons calls for additional proof. This is now confirmed by the shift of the 2LO line frequency, which was taken off-resonance in order to avoid the enhancement of multiple zone-centre LO phonons.

Figure 1 shows that *together* with the shift of TO–TA, an even larger frequency shift of the 2LO line is observed, the maximal shift in this case reaches about 30 cm^{-1}. This spectrum was taken at the interface of the 2.5 μm sample. In figure 2 two Raman spectra of the 3.6 μm sample are shown: the upper spectrum was taken slightly away from the interface, while the lower one was taken within the ZnSe layer further away from the interface. The distances from the interface are apparent from the intensity ratio of the ZnSe and GaAs TO lines, which should also be compared with that in figure 1. In the lower spectrum no shift is observed; this is the regular Raman scattering in the given configuration. In the upper spectrum the TO–TA line frequency shifts by 13 cm^{-1} and that of the 2LO line shifts by 21 cm^{-1}. These frequency shifts should be compared with 18 cm^{-1} and 30 cm^{-1} respectively measured *at* the interface. This proves the tight correlation between the frequency shift of these lines, both measuring the same strain. Two main questions now arise.

(i) What is the origin of this very high strain, which does not seem to be compatible with lattice parameter mismatch? The lattice mismatch between ZnSe and GaAs is only 0.27% and on this basis the LO frequency shift is calculated to be about 1 cm^{-1}; this is also approximately the value reported from conventional Raman scattering results [1] and agrees with our present results obtained in the configuration (1). It should be emphasized that by very high strain we refer here to more than an order of magnitude higher than that estimated from either the LO or TO frequency shift.

(ii) Why is it that a zone-boundary LO phonon appears at a frequency cosiderably higher than expected? Neutron scattering measurements [6] and most of the calculated phonon dispersion as well as second-order Raman scattering measurements [7] placed *all* zone-edge LO phonon frequencies considerably lower than that of $LO(\Gamma)$. The only exception is a calculation [8], where the frequency of LO(L) is about that of $LO(\Gamma)$; from Raman scattering results one is not able, in general, to determine the symmetry of a critical point.

It has already been suggested from TEM measurements [9] and was lately also confirmed by Raman measurements [10] that Ga_2Se_3 is formed at the interface of ZnSe/GaAs. Ga_2Se_3 exhibits an approximate zincblende structure and its lattice parameter is about 5% smaller than these of GaAs and ZnSe. Still, the exact structure of the Ga_2Se_3 or similar compounds formed on the ZnSe/GaAs interface is not completely clear and this includes the lattice parameter. On the grounds of our study, though we cannot determine the size of the islands we can gain some insight, suggesting that these islands are of mesoscopic dimensions. The fact that the second-order lines and the Ga_2Se_3 line [2] are not visibly broadened indicates [11, 12] a size of at least $\sim$ 100 Å, however, dimensions much larger than that will not escape the $k \simeq 0$ measurement. We also assume that the epitaxial Ga_2Se_3 islands are formed with lattice parameter smaller than that of GaAs, but still larger than that of bulk Ga_2Se_3. This accounts for our present results, but calls for more elaborate measurements of both high-resolution TEM as well as of resonant Raman scattering of these Ga_2Se_3 islands. We note that the present results were identical for MOVPE and MBE grown samples. However, the size of the Ga_2Se_3 islands may depend on the quality of the interface and in particular the excess of Ga there. According to this model it is readily understood that ZnSe grown on top of such islands will suffer considerably larger strain, but the order will eventually be restored within the thickness of a few atomic layers. This leaves us with a qualitative model, the details

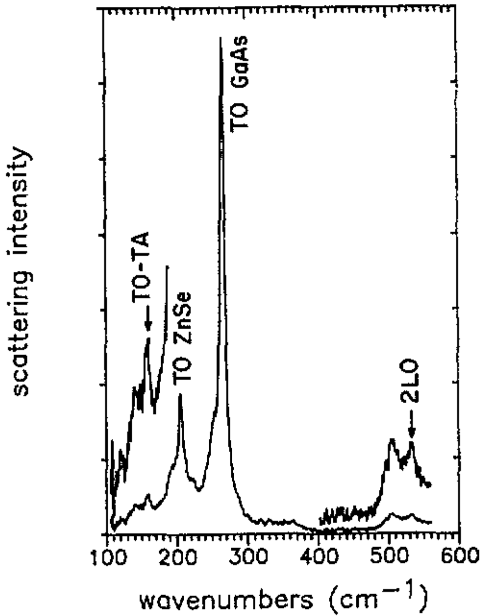

Figure 1. Raman scattering spectrum of ZnSe/GaAs 2.5 μm thick, microprobed at the interface (note the TO line intensity ratio of GaAs and ZnSe), the strain induced shifted TO–TA and 2LO lines are marked by arrows.

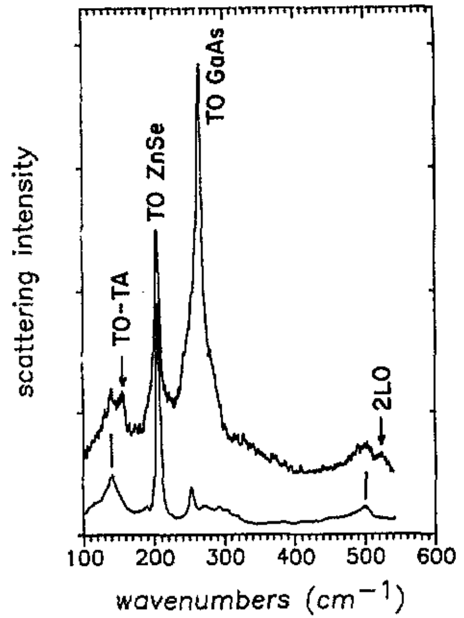

Figure 2. As in figure 1, but for a 3.6 μm thick ZnSe layer, slightly away from the interface (upper spectrum) and further away from the interface (lower spectrum). The vertical bars point at TO–TA and 2LO unshifted frequencies. Note the different TO line intensity ratio of GaAs and ZnSe (also compare to that in figure 1) indicating the distance of the probe from the interface.

of which are still awaiting confirmation. Nevertheless, we do believe that it has been established that such islands of high strain do exist at the interface and that their size must be very small compared with the laser wavelength and large enough to exhibit phonons to scatter the light with significant intensity. The order of 50–100 Å seems to fit both extremes reasonably well, but this cannot be inferred with confidence without further research.

The extrapolation of the TO–TA frequency shift under a hydrostatic pressure of 10 kbar [13] yielded the value of about 36 kbar for the two-dimensional strain. An identical pressure is derived from the frequency shift of the calculated [14] two-phonon subtractive density of states (corresponding to TO–TA) based on neutron scattering data and hydrostatic pressure induced shifts of Raman line frequencies. The decisive check is whether that pressure is also obtained by the frequency shift of the 2LO DOS when compared with that of the calculated [14] two-phonon additive density of states (DOS). It is rewarding to find that this is in fact the case.

However, the frequency value of the highest 2LO DOS is *significantly* lower than the line frequency measured here. It seems that most researchers agree that the frequency of the LO branches at the critical points of both X and L is about 30 cm^{-1} lower than that at Γ. This leaves us with two possibilities: either we are still measuring 2LO(Γ) or that there is a ZB 2LO phonon having about the same frequency. The fact that LO(Γ) hardly shifts excludes entirely the possibility that the harmonic of that line at

zone-centre could shift by 30 cm^{-1}. We are left then with the other possibility that the only data point of the [111] LO phonon branch in the neutron scattering experiment does not define correctly the LO(L) frequency. This is in line with the calculations of Kunc *et al* [8]. The result that the shifts of TO–TA and 2LO are correlated, greatly supports this assignment.

In conclusion, we have shown that the frequency shift of combinational phonons originated at the zone boundary serves as an excellent tool to observe and study microscopic-size islands of different strain from the rest of the epitaxial layer. While frequency shifts of first-order phonons measure the average strain, those of critical point phonons are powerful in measuring phonons restricted to sizes as small as tens of angstroms. The combination of measuring first- and second-order Raman scattering thus gives vital information about the degree of homogeneity in the layer and by the geometry chosen here also that at the interface.

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