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Raman scattering from optical phonons in $InAs_{1-x}Sb_x$/InAs strained-layer superlattices

L. Artús,* R. A. Stradling, Y. B. Li, S. J. Webb, W. T. Yuen, and S. J. Chung
Department of Physics, Blackett Laboratory, Imperial College, London SW7 2BZ, United Kingdom

R. Cuscó
Institut Jaume Almera, Consell Superior d'Investigacions Científiques (CSIC), Lluís Solé i Sabarís s.n., 08028 Barcelona, Spain

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The optical phonon modes of $InAs_{1-x}Sb_x$/InAs strained-layer superlattices with x in the range between 0.14 and 0.39 have been studied by Raman scattering. The observed frequencies of the InAs LO mode agree well with the strain-induced shifts calculated for the InAs layers assuming free-standing conditions. The high quality of the superlattices allows us to observe the InAs-like mode of the alloy. Another peak, whose intensity is dependent on the excitation wavelength, is observed between the InAs LO and TO energies and assigned to interface modes. [S0163-1829(96)08447-0]

During the past few years III-V alloys have been used to develop semiconductor diode lasers emitting in the midinfrared. The $InAs_{1-x}Sb_x$ alloy, which for $x=0.6$ displays the smallest gap in the III-V group, has attracted new interest as a constituent of infrared semiconductor lasers and light-emitting diodes. Recently, it was suggested that the use of compressively strained quantum-well structures could improve the laser operation by reducing Auger recombination,[1] and soon after, the realization of a heterostructure laser emitting at 3.6 μm that incorporated a compressively strained $InAs_{1-x}Sb_x$ active layer was reported.[2] Despite the interest in $InAs_{1-x}Sb_x$/InAs strained-layer superlattices (SLSL's) very little is known about their basic physical properties. In fact, only a magnetophotoluminescence,[3] and a magnetotransmission study[4] of the fundamental band gap have been reported, and yet discrepancies regarding the band alignment inferred from these two studies have arisen. To our knowledge, no study of phonons in $InAs_{1-x}Sb_x$/InAs SLSL's has been published so far. The aim of the present paper is to study the optical modes of these SLSL's in the range from $x=0.14$ to $x=0.39$ by means of Raman spectroscopy.

Undoped $InAs_{1-x}Sb_x$/InAs SLSL's with alloy compositions $x=0.14$, 0.27, 0.32, and 0.39 were grown by molecular-beam epitaxy on semiinsulating (001) GaAs substrates using a VG Semicon V80H three-chamber system. Elemental As, Sb, and In were used as source materials. Following deposition at 580 °C of $\approx$0.3-μm GaAs buffer layer, a 1 μm $InAs_{1-x}Sb_x$ alloy buffer layer with the composition equal to the average composition of the superlattice was grown to relieve the mismatch strain between the GaAs substrate and the superlattice. Then 2 μm superlattices were grown with equal well and barrier thickness, with periods ranging from 80 Å/80 Å to 117 Å/117 Å. The superlattices were grown at 450 °C. At this growth temperature, phase separation that could complicate the interpretation does not occur.[5] *In situ* reflection high-energy electron diffraction oscillations were used to calibrate the group-V fluxes accurately. The alloy compositions were measured by x-ray diffraction.

The Raman spectra were recorded in backscattering configuration from the (001) face using a T64000 Jobin-Yvon spectrometer equipped with a charge coupled device cooled with liquid nitrogen. The measurements were performed at room temperature with resolution better than 1 cm^{-1}. Different lines of an Ar^+ laser were used as excitation, at a power of 150 mW on the sample.

Figure 1 shows the Raman spectra of sample IC389, corresponding to an alloy composition of $x=0.32$, measured in $Z(X,X)Z$ and $Z(X,Y)Z$ configurations in the frequency range of the superlattice optical modes using the 514.5-nm excitation line. X, Y, and Z are defined along the [100], [010], and [001] crystal axes, respectively. In the $Z(X,Y)Z$ configuration the dipole-allowed LO modes have B_2 symmetry, whereas in the $Z(X,X)Z$ configuration the LO modes, of A_1 symmetry, are dipole forbidden, but they become Raman active near resonance due to the intraband Fröhlich interaction.[6] Considering both polarization configurations, four distinct modes can be observed.

The highest energy mode at 234.8 cm^{-1}, although much stronger in the dipole-allowed B_2 symmetry, is observed for both polarizations, and corresponds to the InAs LO mode

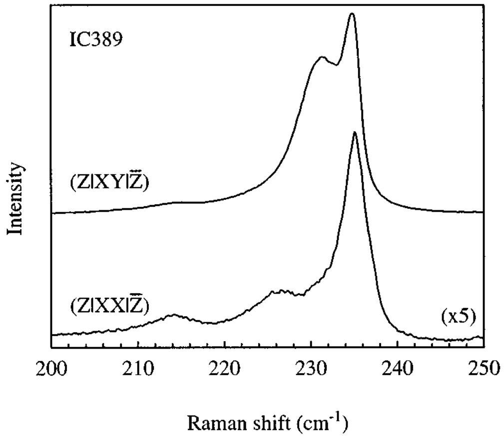

FIG. 1. Raman spectra of sample IC389 ($x=0.32$) in the optical-mode region for $Z(X,X)Z$ and $Z(X,Y)Z$ configurations. The spectra were recorded at room temperature using the 514.5-nm excitation line with resolution better than 1 cm^{-1}.

under tensile strain. To support this assignment we proceed to calculate the strain-induced phonon shifts in the strained layers of $InAs_{1-x}Sb_x/InAs$ superlattices. Lattice mismatch in these superlattices results in a tensile strain in the InAs layers and a compressive strain in the alloy layers. As the whole thickness of the superlattices studied is well above the critical value for substrate-imposed pseudomorphic growth,[7] free-standing strain conditions are assumed. The shift in the LO phonon frequency of each constituent material in a [001]-oriented superlattice is given by[6]

$$\frac{\delta\omega}{\omega}=\tilde{K}_{12}\epsilon_{xx}+\frac{\tilde{K}_{11}}{2}\,\epsilon_{zz}\,, \tag{1}$$

where $\tilde{K}_{mn}$ is a dimensionless fourth rank tensor describing the strain variation of the spring constants. The in-plane and out-of-plane strain components in a layer of the component i of a free-standing SLSL are given, respectively, by[6]

$$\epsilon_{xx}^{(i)}=\left(\frac{a^{(j)}-a^{(i)}}{a}\right)\left(\frac{Q_j d_j}{Q_i d_i+Q_j d_j}\right)\quad (i\neq j),$$

$$\epsilon_{zz}^{(i)}=-\frac{2C_{12}^{(i)}}{C_{11}^{(i)}}\,\epsilon_{xx}^{(i)}\,, \tag{2}$$

where $a^{(i)}$ and $C_{mn}^{(i)}$ are the lattice parameters and the elastic constants of the respective layers, $a=(a^{(1)}+a^{(2)})/2$, d_i is the layer thickness, and $Q_i=2\{C_{11}^{(i)}+C_{12}^{(i)}-(2[C_{12}^{(i)}]^2/C_{11}^{(i)})\}$.

Assuming a linear variation with composition of the elastic constants of the alloy, Eqs. (2) can be used to obtain the values for the strain components in the InAs layer. Experimental values of the elastic constants for InAs ($C_{11}=8.329\times10^{11}$ dyn cm^{-1} and $C_{12}=4.526\times10^{11}$ dyn cm^{-1}) and for InSb ($C_{11}=6.6\times10^{11}$ dyn cm^{-1} and $C_{12}=3.6\times10^{11}$ dyn cm^{-1}) were taken from Ref. 8. Then, Eq. (1) can be used to calculate the strain-induced shift of the LO phonon in the InAs layers. Taking the values $\tilde{K}_{11}=-1.753$ and $\tilde{K}_{12}=-2.323$ for the tensor components of InAs,[9,10] we obtain a relative frequency shift $\delta\omega/\omega=-1.45\times10^{-2}$. Considering the room-temperature, unstrained LO-phonon frequency of InAs to be $\omega_{LO}=238.6$ cm^{-1},[8] the strained LO frequency $\omega_c=235.1$ cm^{-1} obtained from this calculation for the parameters of sample IC389 is in excellent agreement with the experimental LO-mode frequency found at 234.8 cm^{-1} in this sample.

In Fig. 2 we show the Raman spectra obtained from different alloy composition SLSL's in the $Z(X,X)Z$ configuration, using the 514.5-nm laser line excitation. Three modes have been detected for all the different composition SLSL's using this excitation line. The shift of the InAs LO phonon induced by tensile strain in the InAs layers, which increases with the alloy Sb composition, can be clearly observed. In Table I the LO-phonon frequencies for the different SLSL's as determined from our Raman measurements are compared with the values for strained LO modes of InAs calculated using the scheme described above. An excellent agreement has been found for all the samples, which confirms the free-standing strain conditions assumed for these SLSL's. The lowest frequency mode, observed at ≈214 cm^{-1} as a very weak and broad peak in all samples and for the different excitation lines, is assigned to the forbidden TO InAs mode under tensile strain. For the TO mode, the strain-induced shift is given by[6]

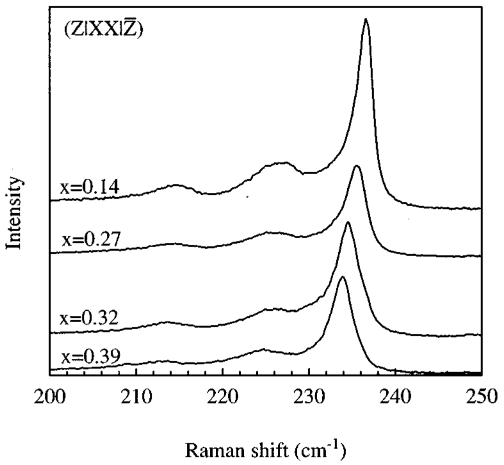

FIG. 2. Room-temperature Raman spectra of $InAs_{1-x}Sb_x/InAs$ SLSL's with different alloy composition, recorded in the $Z(X,X)\bar{Z}$ configuration using the 514.5-nm excitation line.

$$\frac{\delta\omega}{\omega}=\frac{\tilde{K}_{11}^{TO}}{2}\,\epsilon_{xx}+\frac{\tilde{K}_{12}^{TO}}{2}\,(\epsilon_{yy}+\epsilon_{zz}) \tag{3}$$

with $\tilde{K}_{11}^{TO}=-2.04$ and $\tilde{K}_{12}^{TO}=-2.61$.[9,10] For sample IC389, taking the bulk (unstrained) InAs TO frequency to be $\omega_{TO}=217.3$ cm^{-1},[8] this expression yields a frequency shift of $\delta\omega=-2.1$ cm^{-1}, in reasonable agreement with the observed feature.

SLSL's made up of an alloy and the related pure compound can be grouped into two categories depending on the relative shift of the LO modes with strain. One group includes those SLSL's in which the strain increases the energy separation between the LO modes of the constituent layers, hereafter referred to as strain-enhanced phonon separation superlattices. In this group we find, for instance, the $In_{1-x}Al_xSb/InSb$ SLSL's.[11] The other group is composed of those SLSL's in which the strain effect is the reverse, that is, the energy separation between the LO modes of the constituents is reduced by strain, hereafter referred to as strain-reduced phonon separation (SREPS) superlattices. In this group we find, for instance, the $In_xGa_{1-x}As/GaAs$ SLSL, in which the LO peaks corresponding to GaAs and to the GaAs-like mode of the alloy could not be spectrally resolved.[12–14]

The $InAs_{1-x}Sb_x/InAs$ SLSL's studied in the present paper are SREPS superlattices. In fact, the $InAs_{1-x}Sb_x$ alloy was reported to have a two-mode behavior, and the frequency dependence of the LO InAs-like mode on alloy composition was fitted to a linear relationship[15]

$$\omega_{LO}^{\text{InAs-like}}(x)=238-32x\quad(\text{cm}^{-1}). \tag{4}$$

In the case of the present samples, the InAs layers are under tensile strain whereas the alloy layers are under compressive strain. Since the LO mode of unstrained InAs is higher in energy than the LO InAs-like mode of the alloy, the energy separation between the LO InAs-like mode of the alloy and

TABLE I. Comparison between measured and calculated frequencies (in cm^{-1}) of the LO modes of InAs and the LO InAs-like modes of the alloy for the different InAs$_{1-x}$Sb$_x$/InAs strained-layer superlattices with equal well and barrier thickness d.

Sample	x	d (Å)	$\omega_{\mathrm{LO}}^{\mathrm{InAs}}$ (expt.)	$\omega_{\mathrm{LO}}^{\mathrm{InAs}}$ (calc.)	$\omega_{\mathrm{LO}}^{\mathrm{alloy}}$ (expt.)	$\omega_{\mathrm{LO}}^{\mathrm{alloy}}$ (calc.)
IC494	0.14	80	236.8	236.4	234.1	235.2
IC481	0.27	117	235.5	235.1		232.8
IC389	0.32	100	234.8	234.5	231.2	231.9
IC499	0.39	107	234.0	233.7	232.5	230.5

the InAs LO mode is reduced in these SLSL's. In spite of the fact that InAs$_{1-x}$Sb$_x$/InAs SLSL's belong to the SREPS group, a peak very close to the strained-LO InAs peak can be observed in the $Z(X,Y)Z$ spectrum of sample IC389 shown in Fig. 1. This dipole-allowed mode is due to the LO InAs-like phonons of the InAs$_{1-x}$Sb$_x$ alloy layers. To support this assignment we estimate the LO InAs-like phonon frequency in the strained InAs$_{1-x}$Sb$_x$ alloy layers. The strain-induced shift of this peak in relation to the unstrained LO InAs-like frequency given by Eq. (4) is calculated using Eqs. (1) and (2), with values of $\tilde{K}_{mn}$ and C_{mn} obtained by linear interpolation between the corresponding values of the end-point compounds. The values of $\tilde{K}_{11}=-2.439$ and $\tilde{K}_{12}=-3.279$ for InSb were taken from Ref. 16. For sample IC389, Eq. (1) yields a relative shift of 1.8%, and using Eq. (4) we obtain the value of $\omega_{\mathrm{InAs\text{-}like}}^{\mathrm{LO}}=231.9$ cm^{-1} for the strained LO InAs-like mode of the alloy layers in sample IC389, in excellent agreement with the observed peak. The clear resolution of the peaks corresponding to the strained InAs and InAs-like LO modes was possible in sample IC389 not only because of the high resolution used in these measurements but also because of the quality of that particular sample. In sample IC481 the overlapping InAs-like alloy mode could not be resolved from the intense InAs LO peak probably due to a lesser quality of the superlattice and the consequent broadening of the modes. The frequencies of the InAs-like phonons of the alloy for the different composition SLSL's are listed in Table I, where a good agreement between the observed and the calculated frequencies can be seen. In those spectra where only a shoulder could be observed at the alloy InAs-like mode location, a Lorentzian fit was performed to obtain the alloy InAs-like mode frequency with higher accuracy. The best agreement is found for sample IC389, which would be consistent with its higher quality. To our knowledge, this is the first experimental resolution of the LO modes of the pure compound and its related alloy in a SREPS superlattice.

In the $Z(X,Y)Z$ configuration, the InAs-like mode of the alloy was detected independently of the excitation wavelength, whereas this mode was not observed in any of the $Z(X,X)Z$ spectra. In the $Z(X,X)Z$ configuration, the dipole-forbidden A_1 modes become Raman active near resonance due to the intraband Fröhlich interaction. Since the E_1 resonance of the InAs$_{1-x}$Sb$_x$ alloy is expected to be at lower energy than the E_1 resonance of InAs, and, as discussed below, we used excitation wavelengths not far from the E_1 resonance of the InAs, the excitation laser lines were far from the E_1 resonance of the InAs$_{1-x}$Sb$_x$ alloy layers in our experiments. As can be seen in Fig. 1, even though the 514.5-nm line is not far from the E_1 resonance of the InAs layers, the LO InAs mode is much weaker in the $Z(X,X)Z$ than in the $Z(X,X)Z$ polarization configuration. Therefore, it is not surprising that the LO InAs-like modes of the alloy layers, whose E_1 resonance is still farther from the 514.5-nm line, could not be detected in the $Z(X,X)Z$ configuration.

Given that, in the SLSL's studied, the LO-mode frequency of the strained InAs layers is forbidden in the InAs$_{1-x}$Sb$_x$ layers, the LO InAs mode is expected to be confined in the InAs layers, whereas the LO InAs-like alloy mode, whose frequency lies within the InAs LO branch dispersion, can extend through the superlattice.

As can be seen in Figs. 1 and 2 using the 514.5-nm line a peak at ≈226 cm^{-1} is observed in $Z(X,X)Z$ configuration between the TO and LO InAs modes for all the samples. This peak is wider than the peaks corresponding to the LO phonons of InAs and InAs$_{1-x}$Sb$_x$, and is not detected in $Z(X,Y)Z$ configuration. We assign this peak to Raman scattering by interface modes (IF). As can be seen in Fig. 3, where we show the $Z(X,X)Z$ spectra taken from IC389 for different lines of an Ar$^+$ laser, the intensity of the peak at ≈226 cm^{-1} depends on the excitation wavelength. While it is not detected for the shortest wavelengths, it is clearly seen at 514.5 nm, and its intensity is even stronger at 528.7 nm. The intensity enhancement of the IF modes is probably related to the proximity of the E_1 gap of the strained InAs layers, which is expected to be close to the bulk InAs value

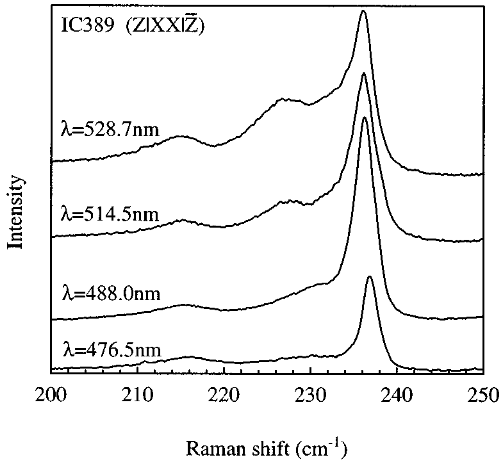

FIG. 3. Room-temperature Raman spectra of sample IC389 for different excitation wavelengths recorded in the $Z(X,X)Z$ configuration.

of 2.46 eV.[17] Contrary to the E_0 resonance in superlattices, for which typical excitonic behavior usually gives rise to a very narrow resonant energy range, interband transitions in superlattices at the E_1 resonance were shown to take place over a much wider energy range.[18] The IF mode is observed at similar frequencies in all the samples. Slight frequency differences may be attributed[6] to the slightly different periods of the samples studied in this paper (see Table I). Further Raman measurements, with tuning of the excitation wavelength, would be required in order to obtain a better knowledge of the E_1 interband transitions in these SLSL's.

Also, the wavelength dependence of the absorption coefficient may play a role in the intensity of the IF modes observed with the 528.7-nm line. The absorption coefficients of InAs and $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ are smaller for the longer wavelength lines.[19] Thus, the intensity of the light reaching the different probed interfaces is higher for the 528.7-nm line. Provided that the incident line is close to resonance, the lower absorption for longer wavelength lines may contribute to the higher intensity of the IF modes detected.

We have studied the optical-mode region of $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$/InAs SLSL's with periods around 20 nm and alloy compositions between 0.14 and 0.39 for different excitation lines. High-resolution Raman measurements have allowed us to resolve the LO InAs-like mode of the alloy and the LO InAs mode, a clear indication of the high quality of the samples. To our knowledge, this is the first time that the LO mode of the alloy has been resolved in a SREPS superlattice. Assuming free-standing strain conditions for these superlattices, the frequencies of the observed LO modes are well accounted for by the strain-induced energy shifts relative to the bulk InAs LO frequency and the $\mathrm{InAs}_{1-x}\mathrm{Sb}_x$ LO InAs-like frequency. The weak, broad mode observed between the InAs TO and LO frequencies, which has been shown to be dependent on the excitation wavelength, is assigned to interface modes.

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[*] Permanent address: Institut Jaume Almera, Consell Superior d'Investigacions Científiques (CSIC), Lluís Solé i Sabarís s.n., 08028 Barcelona, Spain.

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