Quantum-dot phonons in self-assembled InAs/GaAs quantum dots: Dependence on the coverage thickness

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We study the phonons of self-assembled InAs/GaAs quantum dots for different coverage thicknesses L. The additional Raman feature detected between the GaAs transverse optical and the InAs longitudinal optical modes, which we assign to phonons of the dots, exhibits an upward frequency shift with L. This shift is attributed to compressive strain in the dots and, on the basis of its dependence on L, we show that these phonons arise from the quantum dots and not from the wetting layer. © *2000 American Institute of Physics.* [S0003-6951(00)03148-X]

Despite much work dealing with structural and electronic properties of self-assembled quantum dots (QDs)[1] no clear picture of the vibrational properties of the dots has emerged from the few experimental articles reported so far on light scattering of QDs. Theoretical calculations of strain distribution in self-assembled QDs predicted an upward frequency shift of the phonon modes of the dots relative to those of the wetting layer (WL).[2] Carrier relaxation mechanisms involving phonons have been widely reported in self-assembled QD structures. In particular, it has been shown that carrier relaxation is enhanced when the splitting of the energy levels in the QD matches a multiple of the QD phonon energy.[3–5] Therefore, the knowledge of QD phonons is an important subject not only for understanding the fundamental physics of zero-dimensional systems but also because of device applications.

Phonons in different self-assembled QD systems have been studied by means of Raman scattering. A study on uncapped (In, Ga, Al)Sb/GaAs QDs revealed the existence of additional Raman peaks that were assigned to phonons of the QDs, and the absence of the WL signal was explained as being due to its rapid oxidation.[6] In InAs/InP self-assembled QDs Groenen *et al.*[7] observed different Raman peaks in crossed and in parallel polarizations that were assigned to the WL and the QDs, respectively, on the basis of their selection rules. On the other hand, to increase the small Raman-scattering volume of the QDs, InP/InGaP QDs were studied using a forward scattering configuration in a waveguide geometry where the dots are embedded between two thick InAlP cladding layers.[8] Resonant in-plane Raman-scattering measurements showed an additional feature between the InP-like and the GaP-like LO peaks, attributed to phonon contributions from both the InP QDs and the InGaP matrix.

Only two Raman-scattering studies of phonons in InAs/GaAs self-assembled QDs have been reported so far.[9,10] Three Raman features were detected between the transverse optical (TO) and longitudinal optical (LO) modes of GaAs by using an excitation energy close to the $E_0+\Delta_0$ gap of GaAs, and assigned to interface GaAs-like modes localized on the apex of the strained InAs pyramidal dots.[9] Based on this interface mode assignment, the same group has recently reported a topological study of the dots.[10] In the frequency region of the InAs optical phonons, two extremely weak features were detected and assigned to TO and LO phonons of QDs.[9]

In the present letter we provide direct experimental evidence of the existence of phonons arising from the QDs. To demonstrate this point we present a Raman-scattering study of InAs/GaAs QDs for several coverage thicknesses L within the range of coherent three-dimensional (3D) island growth. For all the samples we detect a Raman peak at a frequency higher than the InAs LO frequency that we assign to phonon modes of the QDs and whose frequency exhibits a dependence on L.

The InAs QDs were grown by molecular beam epitaxy on GaAs substrates with (100) crystal orientation. After heating to remove surface oxide, a 0.7 μm GaAs buffer layer was deposited, the first 0.2 μm grown at 580 °C and the remaining 0.5 μm at 600 °C. Before the InAs layers were deposited, there was a growth interrupt while the substrate temperature was reduced to 450 °C. Then an InAs layer of several thicknesses, from 1.4 to 1.9 ML in steps of 0.1 ML, was deposited. Finally, the InAs QDs were capped with 25 nm of GaAs, also grown at 450 °C. Atomic force microscopy characterization of uncapped samples grown under the same conditions showed a dot density of $2\times10^{11}\,\mathrm{cm}^{-2}$, and average diameter and height of 16 and 1.6 nm, respectively, for the sample with $L=1.8$ ML. Previous PL measurements at 5 K on these samples have shown QD emission peaks in the 1.25–1.37 eV range without significant variations in the peak width with L, which confirms the presence of QDs in all the samples studied.[11] Raman-scattering measurements were performed at 80 K with a Jobin-Yvon T64000 spectrometer equipped with a charge coupled device detector. The spectra were recorded in backscattering configuration with very long integration times. We used the 476.5 nm line

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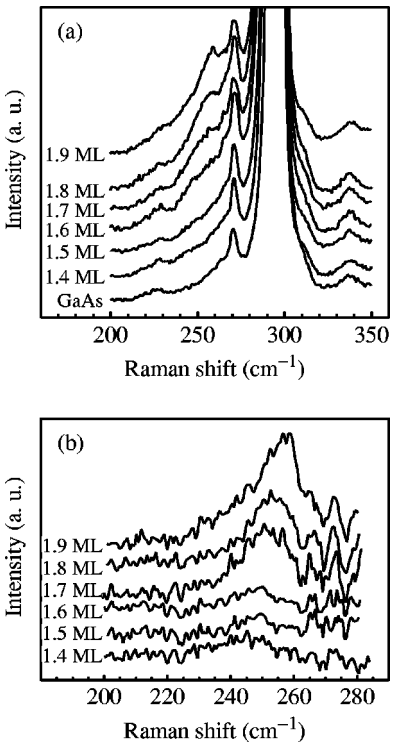

FIG. 1. (a) $x(yz)\overline{x}$ Raman spectra at 80 K of (100) InAs/GaAs self-assembled quantum dots for several coverage thicknesses, compared with the spectrum of bulk GaAs. (b) QD phonon peak after subtraction of the GaAs background.

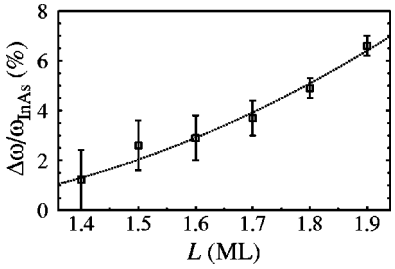

FIG. 2. Plot of the phonon-frequency shifts observed at 80 K in the self-assembled InAs/GaAs QDs, relative to the bulk InAs LO frequency (242 cm^{-1}), as a function of the InAs coverage thickness L. The dotted line is a guide to the eye.

of an Ar^+ laser and the excitation power was kept below 100 mW.

Figure 1(a) shows the Raman spectra of InAs/GaAs QDs with L in the 1.4–1.9 ML range. For comparison we also show the spectrum of a bulk GaAs sample. All spectra display a very intense peak at 295 cm^{-1} corresponding to the GaAs LO phonon mode, which is allowed in the $x(yz)\overline{x}$ polarization ($x\|[100]$, $y\|[010]$, $z\|[001]$), and a weak peak at 270 cm^{-1} corresponding to the GaAs TO phonon mode, which is forbidden in this polarization. Below the GaAs TO peak, the QD samples display an additional feature that shows an upward frequency shift with L. In Fig. 1(b) we plot this spectral region for the QD samples after subtraction of the GaAs background. Despite its very low intensity, the QD peak can be observed even for the samples with the thinnest InAs coverage ($L \approx 1.4$ ML).

Among the lines of the Ar^+ laser, the 476.5 nm excitation line provided the highest QD Raman signal at 80 K. This is probably due to the proximity of the E_1 electronic transition of InAs, which is found at 2.46 eV for the bulk at room temperature.[12] Assuming a temperature dependence similar to that of InSb,[13] we estimate the E_1 energy to be about 2.58 eV for InAs at 80 K. Studies of the E_1-like transition in QDs found energy values close to those of the bulk[14,15] and, consequently, we estimate that the exciting energy we have used is close to the E_1 gap of the InAs/GaAs QDs.

To determine the frequency shifts of the QD phonons relative to the InAs LO mode, we have measured the LO frequency in bulk InAs at 80 K, which we have found to be 242 cm^{-1}. In Fig. 2, we plot the measured shifts of the QD phonon peak relative to the bulk InAs LO mode. Irrespective of the origin of the additional Raman peak, which could arise from the WL or the QDs, the observed upward frequency shifts cannot be due to possible phonon confinement effects, as these would produce a shift to lower energies.[7] The upward shifts cannot either be explained by possible alloying effects due to the diffusion of Ga atoms from the cap and/or the buffer layer into the InAs layer. In fact, phonons in bulk $In_{1-x}Ga_xAs$ have a well-known two-mode behavior and, for $x \leqslant 0.5$, the InAs-like LO modes exhibit a small downward shift in relation to the pure InAs LO mode.[16] Then, the compressive strain induced by the lattice mismatch between InAs and GaAs must be the predominant cause for the upward frequency shift relative to the bulk InAs LO mode. On the other hand, as the Raman features shown in Fig. 1 appear at frequencies lower than the GaAs TO frequency and the spectra were obtained far from GaAs resonances, these features cannot be due to electrostatic interface GaAs-like modes.[17]

A key point in understanding the origin of the phonon modes detected in the self-assembled QD samples is the experimental observation of their frequency dependence on the coverage thickness L, which rules out the possibility that the observed phonons originate in the WL. In fact, for a pseudomorphic strained 2D layer the strain tensor depends on the lattice parameters of the layer and of the surrounding material but not on the layer thickness.[17] Therefore, even in the case where the WL thickness varied with L there would be no change in the strain of the WL. Then the WL phonons should not exhibit any L dependence associated with strain. Moreover, it has been reported that the WL thickness remains constant once the QDs start forming,[18–20] and therefore variations of phonon confinement in the WL are also negligible. Consequently, the observed frequency dependence of the Raman features on L as well as their intensity increase with L are clear indications that they originate in the QDs, and the possibility of a WL origin for these phonons can be ruled out.

Consistent with this, the energies of the InAs/GaAs QDs deduced from the radiative electronic transition measurements that have been reported in the literature are in good agreement with the phonon energies that we have measured. In fact, the phonon energies obtained from resonant PL (30 meV),[3] PLE [31.9 meV,[21] 29 and 32.3 meV (Ref. 4)], and PL [32 meV,[18] 32.3 and 35.7 meV (Ref. 22)] lie mainly between the values of 32.0 and 30.3 meV that we have found, respectively, for the thickest (1.9 ML) and thinnest (1.4 ML) coverages. The value of 35.7 meV reported in Ref. 22, which shows the largest departure from our data, was assigned to an

interface mode. Our results reinforce the hypothesis of phonons with sample-dependent energies participating in the carrier relaxation mechanisms that was suggested in Ref. 4, and confirm that, in fact, differences in the QD phonon energies are found among different samples. The possibility of phonon confinement contributing to the phonon frequency shifts observed for samples with different L cannot be ruled out. However, given the small coverage thickness increments of $\Delta L \approx 0.1$ ML in the series of QD samples, the large frequency shifts observed between consecutive samples cannot be accounted for solely by a decrease of phonon confinement with the size of the QDs as L increases.

Thus, the variation of the QD phonon relative frequency shifts reported in Fig. 2 should contain a substantial contribution from the QD strain dependence on L. The cause of the change in the strain distribution in the QDs is possibly twofold. On the one hand, the shape of the QDs changes with L,[20,23] which implies different strain distributions in the dots.[2] On the other hand, the strain in the dots can be altered by the increasing proximity of the neighboring dots as L increases.[19] As a consequence, the phonon energy of self-assembled QDs is not specific for the compounds forming the QD system, but it also depends on the thickness of the coverage layer.

The QD phonons show a strong polarization dependence as they are observed in the $z(xy)\bar{z}$ but not in the $z(xx)\bar{z}$ configuration, that is, they follow the same selection rules as the LO phonons in bulk zinc-blende semiconductors. This is in disagreement with Raman-scattering experiments reported on InAs/InP QDs.[7] In that work, a mode detected in the $z(xx)\bar{z}$ configuration was assigned to the QD, while a mode observed at a lower frequency in the $z(xy)\bar{z}$ configuration was assigned to the WL on the basis of the E_1 resonance taking place in the 3D like InAs islands but not in the WL, assuming that the E_1 gap is not open in a thin 2D like WL. Nevertheless, E_1 transitions associated to the WL were observed in later electroreflectance studies on these structures.[14] The total absence of Raman signal from the QDs under crossed polarizations could not be explained either. In our Raman spectra, the phonons from the QDs are observed only in crossed polarization, and no Raman signal could be detected from the QDs in parallel polarization, in spite of the high sensitivity of the experimental setup.[24] In accordance with bulk selection rules, where TO modes are forbidden in backscattering on a (100) face, we have not detected any Raman signal corresponding to the TO modes of the dots. In a previous article on InAs/GaAs QDs,[9] an extremely weak feature at 250 cm^{-1}, between 5 and 8 cm^{-1} below the one assigned to the LO modes, was assigned to the TO modes of the QDs. Taking into account that the frequency of the bulk InAs TO mode at low temperature was found to be 220 cm^{-1},[25] this assignment would imply a relative frequency shift for the TO modes of the QDs of more than 13%, much higher than the average value obtained from theoretical models.[2]

In conclusion, we have studied the phonons of capped self-assembled InAs/GaAs QDs by means of Raman scattering for several coverage thicknesses, and we have detected phonons at frequencies between the GaAs TO modes and the InAs LO modes that we assign to phonons of the QDs. The frequency of the InAs/GaAs QD phonons shows an upward shift relative to the bulk InAs LO frequency, which is mainly explained by the compressive strain of the InAs QDs induced by the lattice mismatch with the surrounding GaAs matrix. These results show that the phonon energy of the QDs is not characteristic of the compounds forming the QD system, but it displays an energy dependence on the coverage thickness. This dependence constitutes an experimental evidence that the phonons observed are originated in the QDs themselves as opposed to the WL.

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