Probing the intermixing in In(Ga)As/GaAs self-assembled quantum dots by Raman scattering

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We show that Raman scattering is a sensitive technique for probing the degree of Ga intermixing in In(Ga)As/GaAs self-assembled quantum dots (QDs). The shifts of the QD phonon frequency that we observe are explained by the modification of the strain due to Ga incorporation into the QDs from the GaAs matrix during growth. Using an elastic continuum model, we estimate the average In content of the dots from the QD phonon frequency. The varying amount of intermixing in QDs grown with different In compositions, QD layer thicknesses, growth temperatures, and stacking spacer layer thicknesses are investigated. The Raman data indicate that Ga intermixing is larger for QD samples with low In(Ga)As coverage thickness and/or high growth temperature and, in multilayered systems, for samples with small GaAs spacer layers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2172174]

I. INTRODUCTION

Semiconductor quantum dots (QDs) are of great interest both from a technological and a fundamental point of view. Due to the strong three-dimensional (3D) confinement of carriers in QDs, these nanometer-size structures can be regarded as artificial atoms, providing a range of interesting physical phenomena and great potential for device applications. As predicted theoretically, the reduced density of states associated with 3D carrier confinement in QDs makes these systems excellent candidates for the fabrication of temperature-independent, low threshold current lasers.[1]

Self-assembled QDs (SAQDs) spontaneously form when a critical coverage of a highly mismatched material is deposited on a substrate using suitable growth conditions. Strain is the driving force of this growth mode, known as Stranski–Krastanov (SK), which causes the transition from two-dimensional growth to the formation of defect-free islands.[1] A thin layer of the deposited material, known as the wetting layer (WL), is left under the SAQDs. The fabrication process ends with the capping of the islands so that the resulting QDs are surrounded by a matrix of larger band gap material. Since the self-assembly process removes the need for lithography and etching to obtain the dots, SAQDs have received much attention in the last few years and different systems have been developed and studied. In particular, InAs/GaAs and $In_xGa_{1-x}As$/GaAs SAQDs have been widely investigated because of their applications to GaAs-based optoelectronic devices operating in the 1.3–1.5 μm range relevant for optical fiber communications.[2]

The chemical composition, morphology, and strain of SAQDs, which determine their electronic and optical properties, strongly depend on the growth conditions. It is now clear that the description of InAs/GaAs QD formation in terms of a classical SK growth mode has to be modified because of Ga incorporation from the GaAs substrate into the dots.[3,4] Kegel *et al.*[5] determined the lattice parameter distribution and the vertical composition profile in InAs/GaAs QDs by means of a tomographic x-ray diffraction technique, confirming that the Ga fraction of the dots is significantly enhanced due to Ga/In intermixing during QD formation.[3] The chemical composition of SAQDs also seems to depend strongly on the capping conditions.[6] In the $In_xGa_{1-x}As$/GaAs QD system, segregation effects enhance the In fraction in the QDs at the expense of the WL.[7]

Whereas imaging techniques are routinely used to characterize the shape, size, and density of SAQDs,[1] in general it is difficult to probe the strain and composition of these systems with existing methods.[5,8,9] Thus, the availability of techniques for obtaining information about these QD properties is highly desirable. Vibrational spectroscopies, and in particular Raman scattering, are widely used to investigate the strain and composition of semiconductor materials and structures. However, the scattering volume of the QDs is very small relative to the matrix, and this may have a bearing on the small number of works that have employed Raman scattering to investigate SAQDs[10] as compared to other semiconductor structures. Despite this drawback, it has been shown that Raman scattering may yield valuable information on QD composition and strain depending on the system under consideration.[11–15] For instance, the optical phonon frequencies are particularly sensitive to strain and composition

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in Si/Ge QDs,[15] which allows one to evaluate possible intermixing effects that take place during the growth of the structures. In contrast, the phonon frequency shifts in other QD systems are not very sensitive to alloying effects. This is the case, for instance, of InAsSb/InP QDs due to the compensating effect of the compressive strain introduced by Sb on the downward frequency shift of the InAsSb alloy for increasing Sb composition.[16] For InAs/GaAs and InGaAs/GaAs SAQDs, detailed quantitative analyses of the dependence of the QD phonon frequencies on strain and composition have not been carried out.

In the present work, we use Raman scattering to investigate Ga incorporation into In(Ga)As QDs from the surrounding GaAs matrix for a variety of QD structures and growth conditions. We show that by an analysis of the phonon frequency dependence on strain and composition, a good estimate of the average In composition in the QDs can be readily obtained from the Raman spectra. We investigate several InAs and $In_xGa_{1-x}As$ SAQD systems grown on GaAs substrates. The aim of our study is the assessment of the degree of In/Ga intermixing that takes place during the growth of the QDs. To relate the In fraction in the SAQDs to the QD phonon frequency, we evaluate the average strain in $In_xGa_{1-x}As$ QDs for different x values using an elastic continuum model and then we determine the corresponding strain-induced shift in the phonon frequencies. The resulting phonon frequency versus x curve allows us to evaluate the In content in our samples from the QD phonon frequency values obtained by Raman scattering.

We focus on the following structures: (i) two series of single layers of InAs/GaAs and $In_xGa_{1-x}As$/GaAs QDs grown with different coverage thicknesses; (ii) InAs/GaAs QDs grown at different growth temperatures; and (iii) a series of InAs/GaAs stacked QDs with different spacer layer thicknesses. We find that the average strain in the InAs/GaAs QDs increases with the InAs coverage thickness, which reflects an increase of the average In fraction in the QDs. In contrast, the strain of the $In_xGa_{1-x}As$/GaAs dots, which is strongly reduced relative to the InAs/GaAs dots due to the presence of Ga, depends weakly on the coverage thickness. For InAs/GaAs QDs grown at different temperatures, our results are in agreement with the expected enhancement of Ga intermixing at higher growth temperatures. Intermixing effects are also important in InAs/GaAs stacked QDs, and give rise to an increased Ga content in structures grown with spacer layers less than 50 Å.

II. EXPERIMENT

All the SAQD samples studied in this work were grown by molecular beam epitaxy on (001) GaAs substrates. Table I gives details of the QD growth temperature (T_G), the coverage thickness (L), and the nominal composition of the QDs. The peak energy (E_{PL}) of the QD photoluminescence (PL) emission at 4.2 K is also listed in the table.

Samples A1–A6 consist of a single layer of InAs grown on (001)-GaAs with a coverage thickness L equal to 1.4, 1.5, 1.6, 1.7, 1.8, and 1.9 monolayers (MLs), respectively. All these samples contain QDs, as shown by PL and reflection high-energy electron difraction (RHEED) results reported in Ref. 17. Samples B1–B3 consist of a single layer of $In_{0.5}Ga_{0.5}As$ grown on (001)-GaAs with L=0.7, 1.1, and 1.7 nm. As shown in Ref. 17, only samples B2 and B3 contain QDs, while the RHEED pattern for sample B1 corresponds to a two-dimensional (2D) wetting layer. Samples C1–C3 contain a single layer of InAs QDs (L=1.8 ML) grown on (001)-GaAs at T_G=450, 480, and 520 °C, respectively. Samples D1–D5 consist of ten layers of InAs/GaAs QDs with GaAs spacer layers of thickness d=98, 55, 31, 17, and 14 Å, respectively. All samples were capped with 25 nm of GaAs, grown at the same temperature as the QDs. The growth rate for the structures containing InAs and $In_{0.5}Ga_{0.5}As$ QDs was 0.062 ML/s and 0.018 nm/s, respectively.

TABLE I. InAs/GaAs and $In_{0.5}Ga_{0.5}As$/GaAs QD structures studied in this work. The growth temperature (T_G), coverage thickness (L), and PL peak energy (E_{PL}) are listed for all samples. Sets A, B, and C consist of samples containing a single layer of QDs. Samples D1–D5 contain ten layers of QDs with GaAs spacer layers of thickness d.

Sample	Sample structure	T_G (°C)	L	E_{PL} (eV)
A1	InAs/GaAs	450	1.4 ML	1.37
A2	InAs/GaAs	450	1.5 ML	1.32
A3	InAs/GaAs	450	1.6 ML	1.30
A4	InAs/GaAs	450	1.7 ML	1.26
A5	InAs/GaAs	450	1.8 ML	1.25
A6	InAs/GaAs	450	1.9 ML	1.25
B1	$In_{0.5}Ga_{0.5}As$/GaAs	450	0.7 nm	1.39
B2	$In_{0.5}Ga_{0.5}As$/GaAs	450	1.1 nm	1.29
B3	$In_{0.5}Ga_{0.5}As$/GaAs	450	1.7 nm	1.20
C1	InAs/GaAs	450	1.8 ML	1.25
C2	InAs/GaAs	480	1.8 ML	1.24
C3	InAs/GaAs	520	1.8 ML	1.14
D1	InAs/GaAs (d=98 Å)	450	1.8 ML	1.22
D2	InAs/GaAs (d=55 Å)	450	1.8 ML	1.15
D3	InAs/GaAs (d=31 Å)	450	1.8 ML	1.05
D4	InAs/GaAs (d=17 Å)	450	1.8 ML	1.06
D5	InAs/GaAs (d=14 Å)	500	1.8 ML	1.09

Raman scattering measurements were carried out with the macroconfiguration of a Jobin–Yvon T64000 spectrometer equipped with a charge coupled device detector. The spectra were acquired at 80 K in a backscattering geometry, along the [001] direction, using different lines of an Ar^+ laser. Due to the weak Raman signal of the QDs, long integration times (2–3 h depending on the sample) were used. The incident power on the samples was kept below 100 mW.

III. QD OPTICAL-PHONON FREQUENCY VERSUS IN CONTENT

The frequency of QD phonons depends on the composition and shape of the QDs and on the strain field induced by the lattice mismatch with the surrounding matrix. Because of the high lattice mismatch between the In(Ga)As QDs and the GaAs matrix, strain gives rise to strong frequency shifts of the QD phonons relative to the bulk. In turn, lattice mismatch is determined by the QD composition, which may be significantly altered by Ga intermixing effects taking place during the QD growth. Therefore, changes in the In fraction of the QDs also affect the QD phonon frequencies through changes in the strain field of the dots. Both effects need to be taken into account in the analysis of the QD phonon data. On the other hand, QD phonon frequencies may also be affected by phonon confinement effects. However, for typical QD sizes these effects are small and can be neglected. A rough estimate of the confinement-induced shifts using the linear chain model[18] yields values lower than ≈ 0.5 cm^{-1} for the QD sizes of the samples studied in this work.[11,14]

The frequency of optical phonons in strained QDs can be calculated following the approximation proposed in Ref. 11, where it is assumed that the vibrational eigenmodes involving all the atoms inside the dots experience the average QD strain field. The use of this approximation for our SAQDs is justified since the strain distribution varies smoothly inside the QDs, as indicated by elastic continuum calculations.[8] Then, assuming an average In fraction x, which is the same for all islands, the frequency of the longitudinal optical (LO) QD phonons propagating along the [001] direction of the strained $In_xGa_{1-x}As/GaAs$ QDs is given by[11,18]

$$\omega_{\mathrm{LO}}^{\mathrm{QD}}(x) = \omega_{\mathrm{LO}}^{0}(x)\left[1 + \tfrac{1}{2}\widetilde{K}_{12}(\bar{\epsilon}_{xx} + \bar{\epsilon}_{yy}) + \tfrac{1}{2}\widetilde{K}_{11}\bar{\varepsilon}_{zz}\right], \tag{1}$$

where $\bar{\epsilon}_{ij}$ are the averaged values of the strain field components in the QDs, $\widetilde{K}_{ij}$ are the dimensionless phonon deformation potentials, and $\omega_{\mathrm{LO}}^{0}(x)$ is the frequency of the corresponding mode of bulk unstrained $In_xGa_{1-x}As$. There is some controversy in the values of $\widetilde{K}_{ij}$ reported for InAs.[19] Following the discussion of Ref. 11, we take $\widetilde{K}_{12}=-2.43$ and $\widetilde{K}_{11}=-1.50$ for the LO phonon mode of InAs. For the LO phonon mode of GaAs, we take $\widetilde{K}_{12}=-2.7$ and $\widetilde{K}_{11}=-2.0$.[18] For $In_xGa_{1-x}As$, we take values that vary linearly from those of pure InAs to those of pure GaAs.

To obtain the QD phonon frequency from Eq. (1), we need to evaluate the strain field of the $In_xGa_{1-x}As$ QDs. This was done within the elastic continuum model, which has been shown to provide an accurate representation of the strain within a cleaved SAQD,[8] using the finite-element calculation package *ABAQUS*.[8,20] We model the QDs using a specific geometry, namely a square-based truncated pyramid, with 36×36 nm^2 base, 2 nm height, and 33×33 nm^2 top face. This large ratio between the lateral size and height of the dots is indicated by atomic force microscopy (AFM) characterization of our samples.[17] As discussed later in this section, for this flat geometry of the dots, the precise dimensions do not significantly affect either the average strain or the determination of the phonon frequencies. Although the actual WL thickness has little effect on the calculated QD strain distribution and only affects the electronic structure of the dots,[21] we also included a thin WL in the QD model. In our calculations, we introduce lattice mismatch strain by setting the corresponding thermal expansion coefficient for the QD material and for the matrix.[20] The lattice mismatch strain is assumed to depend linearly on x. In the elastic continuum model of the QDs, the Young's modulus E and the Poisson ratio ν take different values inside and outside the QDs. For InAs, we use $E_{\mathrm{InAs}}=51.44$ GPa and $\nu_{\mathrm{InAs}}=0.353$; for GaAs, we take $E_{\mathrm{GaAs}}=85.62$ GPa and $\nu_{\mathrm{GaAs}}=0.318$. A linear variation of both E and ν with composition is assumed for $In_xGa_{1-x}As$.

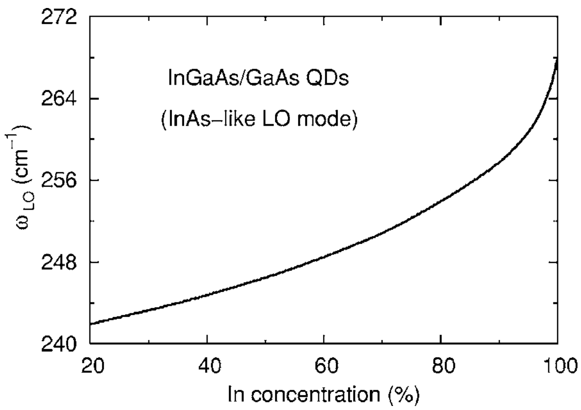

FIG. 1. Calculated dependence of the QD phonon frequency of (InGa)As/GaAs self-assembled QDs as a function of the average In fraction of the dots. The calculated QD phonon frequency depends very little on the particular QD geometry considered for the calculations.

From the calculated QD strain field, we obtain the average values of the strain tensor components $\bar{\epsilon}_{ij}$ by integration over the whole QD volume. Because of the x-y symmetry of the QD model, we have $\bar{\epsilon}_{xx}=\bar{\epsilon}_{yy}$, and $\bar{\epsilon}_{ij}=0$ for $i \neq j$.

To calculate the QD phonon frequency as a function of x using Eq. (1), we have considered the composition dependence of the frequency of the LO phonon modes of bulk, unstrained $In_xGa_{1-x}As$. This can be done by using the model proposed in Ref. 22 to explain the two-mode optical-phonon behavior of bulk $In_xGa_{1-x}As$. While the GaAs-like LO phonon mode of unstrained $In_xGa_{1-x}As$ exhibits a frequency decrease with x,[22] the lattice mismatch between the QDs and the GaAs matrix gives rise to a strain-induced shift to higher frequencies of the QD GaAs-like LO mode; this shift increases with x. The GaAs-like LO mode frequency in the strained $In_xGa_{1-x}As$ QDs lies in the vicinity of the LO mode of GaAs because both effects, composition and strain, roughly compensate each other. Thus, this mode is masked in the Raman spectra by the strong overlapping GaAs LO phonon peak of the matrix. In contrast, observation in the Raman spectra of the InAs-like LO branch of the strained $In_xGa_{1-x}As$ QDs is possible because its frequency lies well below the transverse optical (TO) phonon frequency of GaAs. Note that the InAs-like branch of unstrained, bulk $In_xGa_{1-x}As$ shows only a slight dependence on composition,[22] and as a consequence the frequency of the InAs-like LO frequency of the QDs is mainly governed by the strain of the QD material, which depends on the In fraction of the QDs.

Figure 1 shows the calculated frequency of the InAs-like LO phonons as a function of the In fraction for the QD geometry considered, obtained with the model described above. As expected, the calculations clearly show that $\omega_{\mathrm{LO}}^{\mathrm{QD}}(x)$ is reduced when the In fraction x in the QDs is decreased, reflecting the reduction of the average strain in the QDs. For $x \to 0$, $\omega_{\mathrm{LO}}^{\mathrm{QD}}(x)$ approaches the frequency of the In–As local vibrations in GaAs.[22] The fact that for $x \to 1$ the curve becomes appreciably steeper is a consequence of the rapid increase of $\sim$5 cm^{-1} that the InAs-like LO branch of bulk $In_xGa_{1-x}As$ exhibits toward the InAs end.[22] As can be seen in Fig. 1, the InAs-like LO phonon frequency of the QDs is very sensitive to composition variations, and therefore frequency shifts of the QD phonon peak observed in the Raman spectra can be used to probe the average composition inside the QDs.

The curve shown in Fig. 1 was calculated for QDs with a flat and truncated-pyramid geometry, as described above. For such dots, the average strain is expected to be rather insensitive to variations in the dot dimensions. In fact, as suggested in Ref. 11, the limiting case of 2D pseudomorphic $In_xGa_{1-x}As$ is a good approximation for the calculation of QD phonon frequencies in this type of dot. We have repeated the calculation of the InAs-like LO frequency for a 2D pseudomorphic layer and we find phonon frequencies which are less than 1.3 cm^{-1} higher than the results shown in Fig. 1. Such small differences lie within the experimental error of the QD phonon frequency determination from the Raman measurements. We have also calculated the InAs-like phonon frequencies of QDs with a significantly different aspect ratio compared to that considered above. For this purpose, we have taken the QD geometry reported in Ref. 8, where the QDs are modeled by truncated pyramids with 18×18 nm^2 base, 5 nm height, and 10.7×10.7 nm^2 top face. For this QD geometry, the resulting QD phonon frequencies are only slightly lower than those plotted in Fig. 1, with differences smaller than $\approx$1 cm^{-1} over the whole In composition range. As expected, the greatest differences occur for $x\rightarrow1$, where the lattice mismatch is higher and therefore the differences in strain distribution among the different QD models are more important.

These results indicate that the variations in QD dimensions usually found for SAQDs with different origins/growth conditions do not have a sizable effect on the QD phonon frequency. Therefore, the frequency shifts observed in the InAs-like LO mode of the QDs can be ascribed mainly to QD composition variations inducing changes in the strain field, and these shifts can be used to probe the average composition of the dots. Thus, by using the ω_{LO}^{QD} versus x curve given in Fig. 1, the average In fraction in the $In_xGa_{1-x}As/GaAs$ QDs can be obtained from the experimentally determined QD phonon frequency.

IV. RESULTS AND DISCUSSION

At the temperatures generally used to grow SAQDs, additional material is incorporated into the dots from the WL and the GaAs substrate.[3] This results in the composition of the islands being different from that of the deposited material. Probing the actual QD composition is difficult, and for InAs/GaAs SAQDs Ga fractions of about 30% and higher were derived from scanning tunneling microscopy[3] and from the analysis of the x-ray intensity distribution in reciprocal space.[5] The Ga composition of the dots may be substantially increased when they are overgrown with a GaAs capping layer.[23]

In the preceding section we have shown that Ga incorporation into the QDs has a strong influence on the QD phonon frequency, and we have evaluated the expected InAs-like LO frequency of the QDs for a range of In fractions. Here we experimentally determine by Raman scattering the QD phonon frequency for a number of different In(Ga)As/GaAs SAQD systems obtained under different growth conditions. Analysis of the data using the model presented in Sec. III allows us to infer the average Ga composition of the dots and thus the degree of intermixing which takes place during the growth of the different SAQD systems studied.

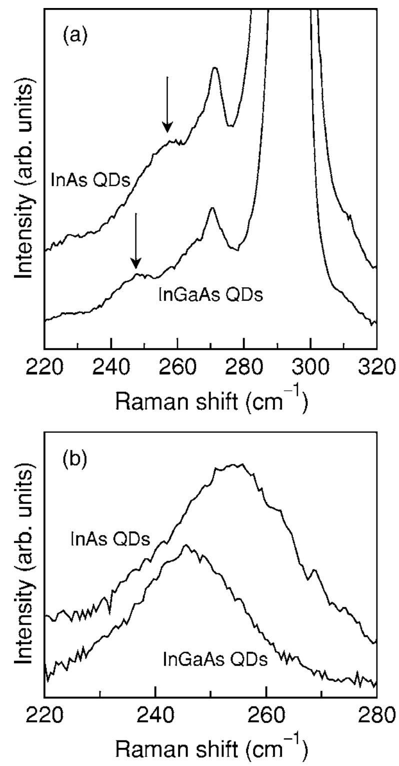

FIG. 2. (a) $z(xy)\bar{z}$ Raman spectra at 80 K of (001) InAs/GaAs and $In_{0.5}Ga_{0.5}As/GaAs$ self-assembled QDs with a coverage thickness of 1.8 ML and 1.7 nm, respectively. The arrows indicate the phonon peaks due to the QDs. (b) QD phonon peaks after subtraction of the GaAs Raman peaks.

A. $In_xGa_{1-x}As$ QDs versus InAs QDs

The critical thickness (L_c) for self assembly of $In_xGa_{1-x}As/GaAs$ QDs is higher than that for InAs/GaAs QDs. This is because the lattice mismatch, and therefore the accumulated strain energy, is lower in 2D $In_xGa_{1-x}As$ layers grown on GaAs than in InAs layers grown on GaAs. Since the QD formation is governed by strain, the reduction of elastic energy is probably the main driving force for Ga intermixing from the GaAs matrix into the QDs.[5] This results in a higher degree of Ga intermixing in InAs QDs than in $In_xGa_{1-x}As$ QDs due to the higher lattice mismatch of InAs deposited on GaAs. On the other hand, segregation effects occur in $In_xGa_{1-x}As$ QDs, which give rise to In enrichment in the QDs at the expense of the WL.[7] It should be emphasized that the intermixing and segregation processes, and thus the final QD composition, may be very sensitive to the growth parameters and subsequent capping.

Figure 2(a) shows $z(xy)\bar{z}$ $(x\|[100], y\|[010], z\|[001])$ Raman spectra from two samples, one containing nominally pure InAs QDs grown on GaAs (sample A5, see Table I) and another containing $In_{0.5}Ga_{0.5}As/GaAs$ QDs (sample B3). Both spectra display a very intense peak at 295 cm^{-1} corresponding to the GaAs LO phonon mode, which is allowed in the polarization configuration used to acquire the spectra, and a weak peak around 270 cm^{-1} corresponding to the GaAs TO phonon mode, forbidden in this polarization geometry. At energies below that of the GaAs TO phonon peak, both samples display an additional feature that does not appear in the Raman spectrum of bulk GaAs [see arrows in Fig. 2(a)]. This feature is assigned to the InAs LO-like QD phonon on the basis of its frequency position and selection rules.[13,14]

The QD peak in the sample containing $In_{0.5}Ga_{0.5}As$ QDs is clearly shifted to lower frequencies with respect to the peak that appears in the InAs QD sample. As discussed in Sec. III, this frequency shift is attributed to the higher Ga content in the $In_{0.5}Ga_{0.5}As$ QDs, which implies a lower average strain in the dots.

Although the QD peaks are well separated from the LO and TO GaAs modes and can be directly observed in the Raman spectra, they are superimposed on a much larger background signal from the GaAs matrix. To improve the accuracy in the determination of the QD phonon frequency, the GaAs background was subtracted from the Raman spectra. Figure 2(b) shows the corresponding QD phonon peaks after background subtraction, from which we determine QD LO phonon frequencies of 246 and 254 cm^{-1} for the $In_{0.5}Ga_{0.5}As/GaAs$ and InAs/GaAs QD samples, respectively.

Using the $\omega_{LO}^{QD}(x)$ curve reported in Fig. 1, we estimate that the average In content of the QDs in the $In_{0.5}Ga_{0.5}As/GaAs$ sample (B3) is $x \approx 0.45$, a value that is close to the nominal composition of the deposited material. This suggests that Ga intermixing takes place to a lesser extent in $In_xGa_{1-x}As$ QDs due to the lower strain energy accumulated in the dots. Furthermore, In segregation effects may be partly compensating the Ga incorporation from the matrix, resulting in an average QD composition that does not show significant deviations from the nominal values. Taking into account the uncertainty associated with the determination of the QD phonon frequency from the rather weak and broad Raman peaks of the QDs, we estimate that the In fraction for samples B3 and A5 has an error bar of about ±0.05.

For the InAs/GaAs sample (A5), the QD phonon peak is located at ≈ 14 cm^{-1} below the expected frequency for pure InAs/GaAs QDs, and according to Fig. 1, the measured QD phonon frequency corresponds to $x \approx 0.8$. These results clearly indicate that the InAs QDs are not pure but contain a significant amount of Ga atoms that are incorporated from the GaAs matrix during the self-assembly process. The large frequency shift of the QD phonons when Ga incorporates into the QD material makes Raman scattering a sensitive tool to assess the degree of intermixing in the In(Ga)As/GaAs SAQD systems.

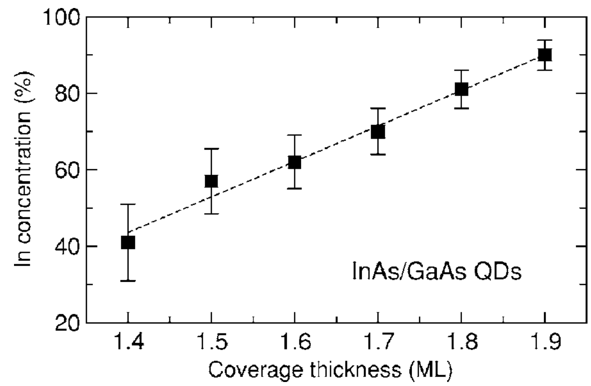

FIG. 3. Plot of the average In concentration of InAs/GaAs self-assembled QDs, determined from the experimental values of the QD phonon frequency and the curve displayed in Fig. 1, as a function of the InAs coverage thickness L for samples A1–A6.

B. InAs/GaAs and $In_xGa_{1-x}As/GaAs$ QDs: dependence on the coverage thickness

It is well known that the properties of QDs depend on the thickness L of deposited material.[17,24] The dependence on L of QD phonons in InAs/GaAs SAQDs was investigated in Ref. 13, where changes in the compressive strain of the InAs QDs as a function of L were reported. Here we revisit those results in the light of the model discussed in Sec. III, which allows us to identify the origin of the strain variations and to evaluate the In content of the InAs/GaAs QDs as a function of L. We analyze the same set of structures that were used in Ref. 13 (samples A1–A6 of Table I), which consist of a single layer of InAs/GaAs QDs grown with L in the 1.4–1.9 ML range. For comparison, we also investigate a set of $In_{0.5}Ga_{0.5}As/GaAs$ QDs with L=0.7, 1.1, and 1.7 nm (samples B1–B3, respectively).

In Fig. 3 we plot the In fraction of the InAs/GaAs QD samples A1–A6 as a function of L, as determined from the measured QD phonon frequencies[13] and the $\omega_{LO}^{QD}(x)$ curve reported in Fig. 1. For the sample with L=1.4 ML (sample A1), with a coverage thickness only slightly above the critical thickness,[17] we find that the In content of the QDs is as low as ≈40%. The In fraction then increases almost linearly with increasing L, and reaches a value of ≈90% for L=1.9 ML (sample A6). Therefore, the QD phonon frequency shifts observed in these samples[13] can be attributed to a decrease in the degree of Ga intermixing with increasing coverage thickness. The fact that the In content of the dots increases with L is related to the high Ga content of the QDs for $L \approx L_c$, which originates from a strong intermixing at the onset of the self-assembly process. It should be noted that for the lowest coverage thicknesses, phonon confinement effects might affect the QD phonon frequency. However, these effects are difficult to evaluate without a precise knowledge of the QD sizes. While phonon confinement may play a role in the QD phonon frequency shifts, rough estimations based on the linear chain model suggest that the QD phonon shifts observed in the samples with the lowest L cannot be accounted for solely by QD size variations. Therefore, although the In fraction of the QDs may be underestimated in these cases by neglecting phonon confinement effects, a sizable change in the In/Ga ratio must occur in the QDs when the coverage is increased from 1.4 to 1.5 ML. For L well above L_c, the additional amount of InAs deposited reduces the average Ga content of the QDs even further, which increases their average strain and induces an upward frequency shift of the QD phonon that can be detected by Raman measurements.

In contrast, our $In_xGa_{1-x}As/GaAs$ QD samples with nominal composition $x=0.5$ did not show any sizable variation of the QD phonon frequency with coverage thickness. The Raman spectrum of the $In_xGa_{1-x}As/GaAs$ QD sample with $L=1.7$ nm (sample B3) is displayed in Fig. 2. A similar spectrum was obtained from the sample with $L=1.1$ nm (sample B2), which showed a QD phonon peak at about the same frequency, but with a reduced intensity. As discussed in Sec. IV A, the QD phonon frequency measured for these samples corresponds to an In fraction of $x\approx 0.45$, which indicates that neither Ga intermixing nor its dependence on coverage thickness have a significant effect on the average composition of these QDs. Thus, the reduction of the PL peak energy observed in sample B3 relative to sample B2 (see Table I) must be a consequence of a size increase of the dots, which lowers the electronic confinement but leaves the QD phonon frequency unaffected as discussed in Sec. III. The coverage thickness for sample B1 ($L=0.7$ nm) is below the critical thickness $L_c\approx 1.1$ nm, and therefore this sample does not contain QDs.[17] The Raman spectrum of sample B1 exhibits an extremely weak feature in the InAs-like LO frequency region. Although we could not obtain a reliable determination of its frequency due to the weak signal, a downward frequency shift relative to samples B2 and B3 was apparent from the direct comparison of the Raman spectra. Such a frequency shift may be a consequence of a higher degree of Ga intermixing in the pseudomorphic 2D $In_xGa_{1-x}As$ layer and/or of phonon confinement effects in the 2D layer.[11]

C. InAs/GaAs QDs: dependence on growth temperature

Substrate temperature has a marked effect on the growth of SAQD structures. Large variations of QD size have been reported for InAs/GaAs QDs grown at different temperatures,[3] which imply a significant dependence of the mass transport from the WL and the substrate on the growth temperature, T_G. Here, we investigate by Raman scattering the degree of Ga intermixing in InAs/GaAs QD samples grown at different temperatures. For this purpose, InAs/GaAs QD structures were grown with $L=1.8$ ML at T_G=450, 480, and 520 °C (samples C1, C2, and C3 of Table I, respectively). All samples were capped with 25 nm of GaAs, grown at the same temperature as the QDs. The growth temperature of the final capping GaAs layer also affects the In composition of these QD structures, since substantial intermixing takes place during the capping stage.

Figure 4 displays the frequency versus T_G of the QD LO phonon peak of these samples, determined from the Raman spectra after subtraction of the GaAs background. As can be seen in Fig. 4, the frequency of the QD phonon peak is the same at 450 and 480 °C. This is in good agreement with the

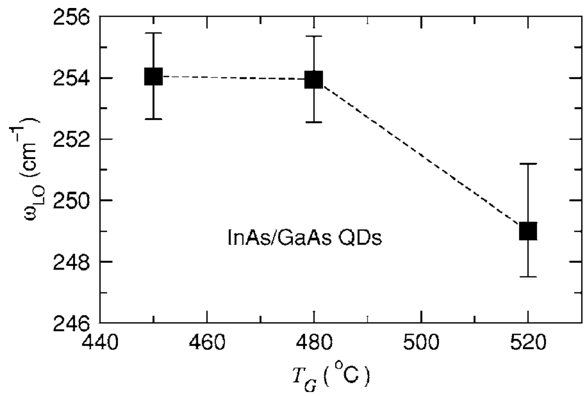

FIG. 4. Plot of the QD phonon frequency observed at 80 K in samples containing InAs/GaAs QDs ($L=1.8$ ML) as a function of the growth temperature T_G (samples C1, C2, and C3).

PL data obtained from these two samples (see column V of Table I), which show no sizeable variations in the PL peak energy from 450 to 480 °C. In contrast, for a growth temperature of 520 °C, both the PL emission energy and the QD phonon frequency exhibit a considerable redshift. The observed redshift in the QD phonon frequency, of about 5 cm^{-1}, must arise from an increase in the Ga content in the sample grown at 520 °C. As discussed in Sec. III, this shift is too large to be explained by any change in QD size. From Fig. 1, we determine that the average In content in this sample is ≈60%, which is substantially lower than for the samples grown at lower T_G. This is in agreement with scanning tunneling microscopy experiments on InAs/GaAs QDs,[3] which showed that increasing the substrate temperature yields QDs with greater volume due to incorporation of Ga from the substrate. Although this incorporation of Ga into the QDs is expected to blueshift the PL emission, the increase in QD size, which lowers the electronic energy levels, may compensate for such a blueshift and thus explain the reduction of the PL peak energy that we observe in the sample grown at 520 °C.

D. InAs/GaAs stacked QDs

The strain fields induced by the 3D islands in the spacer layers are the driving force for vertical self organization in stacked QD structures. The evolving strain fields determine the size and distribution of the QDs in the multilayered structures, and in turn, also affect their optical properties. We have recently shown that the strain in stacked QD structures can be probed by Raman scattering.[14] We found that the frequency of the QD phonon peak decreases as the spacing between QD layers is reduced in samples containing ten layers of InAs/GaAs QDs. These frequency shifts were attributed to the strain relaxation that takes place during the growth of the QD multilayer system. Using the model described in Sec. III, the strain variations observed in Ref. 14 can now be linked to changes in the average In content in the dots.

In Fig. 5, we plot the In fraction as determined from the measured QD phonon frequencies[14] and the $\omega_{LO}^{QD}(x)$ curve of Fig. 1 for the stacked InAs/GaAs QD samples investigated in Ref. 14. These consist of ten layers of InAs/GaAs QDs

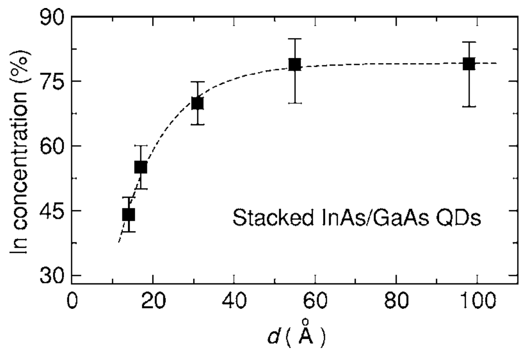

FIG. 5. Plot of the average In concentration of InAs/GaAs stacked QDs (ten layers), with GaAs spacer layers of thickness d, as a function of d (samples D1–D5).

with GaAs spacer layers of thickness d ranging from 98 down to 14 Å (samples D1–D5 of Table I, respectively). By using the curve of Fig. 1 to obtain the average In content of the samples, we implicitly assume that the frequency of the QD phonons is unaffected by the presence of the neighboring QD layers. This assumption is strictly valid only for the uncoupled dot layers obtained for the highest values of d. In general, vertical self organization of stacked QD structures requires strain field interaction among the layers during their growth, and such interaction is expected to lower the frequency of QD phonons. However, elastic continuum model calculations indicate that the QD phonon frequency is not substantially affected by stacking alone. This can be shown by applying the finite element model described in Sec. III to calculate the average strain in a multilayered system consisting of ten identical layers of InAs/GaAs QDs. The resulting QD phonon frequencies, calculated with Eq. (1), show variations with d which are much smaller than those observed experimentally,[14] even for the smallest spacings. As a consequence, the frequency shifts observed in samples D1–D5[14] must occur mainly due to elastic strain relaxation of the QDs induced by Ga intermixing taking place during the self-assembly process and also during the growth of the GaAs spacer layers and the final capping layer.

On the other hand, it must be pointed out that the incorporation of In into the GaAs matrix due to In/Ga intermixing might contribute to the strain relaxation observed in our samples. However, the volume of deposited InAs is much lower than the GaAs volume deposited in the spacer layers, and this limits the total amount of In ions that may incorporate into the GaAs matrix. Even in the sample with the lowest d value (sample D5), the InAs coverage thickness is still more than two times smaller than the spacer layer thickness, and therefore the overall incorporation of In to the spacer layer must be small.

Then, the average In fraction of the stacked QDs can still be inferred from the QD phonon frequency using the curve of Fig. 1. As shown in Fig. 5, our results indicate that the average In content of the dots is greatly reduced in closely spaced QD layers. We find In fractions of about 50% for a spacer layer thickness $d=17$ Å, and of 45% for $d=14$ Å. We note that the latter was grown at a higher temperature and this may have also contributed to its high Ga content. The high degree of Ga intermixing in these two samples is consistent with the PL data reported in Ref. 14, which shows a blueshift of the PL emission that can neither be attributed to electronic coupling nor to the relaxation of strain due to interlayer interaction. The present analysis shows that the origin of the observed PL blueshift is the Ga incorporation into the QD material during the self-assembly process.

Finally, we would like to make a remark about the estimation of the strain from the measured frequencies of the LO phonon peaks. If, as in Ref. 14, one assumes pure InAs QDs, the derived strain values are significantly lower than those obtained by using the actual QD composition. This is a consequence of the particular compositional dependence of the LO InAs-like frequency of bulk $In_xGa_{1-x}As$ which, as noted in Sec. III, is rather flat over a wide range of alloy compositions, but exhibits a steep increase of about 5 cm^{-1} toward the InAs end. Thus, if pure InAs QDs are assumed, the Raman frequency of the unstrained material is overestimated by $\sim$5 cm^{-1}, which leads to underestimating the strain-induced shift and hence to deducing lower average strain values from the experimental phonon frequencies. This emphasizes the importance of knowing the actual composition of the QDs to understand the origin of the Raman shifts and calculate the strain field of the dots.

V. SUMMARY

We have shown that Raman scattering is a powerful tool for assessing the degree of (In,Ga)As alloying in In(Ga)As/GaAs QD structures. We have studied the QD InAs-like LO phonon in a number of SAQD samples grown under different conditions. Systematic variations of the QD phonon frequency have been observed which depend on the growth parameters.

A simple QD model based on continuum elasticity theory has allowed us to identify the variations of strain associated with changes in QD composition as the main cause of the observed QD phonon frequency shifts. While in some cases other effects such as phonon confinement in small dots or interlayer strain field coupling in stacked QD structures may contribute to the QD phonon shifts, such contributions are generally small and amount only to a slight underestimation of the In content of the dots. The model yields a QD phonon frequency versus In fraction curve that can be generally used to obtain the average In content of the QD material for a variety of In(Ga)As/GaAs SAQD structures.

Our Raman scattering results show that strong Ga intermixing effects take place in InAs/GaAs QDs. The actual composition of the QDs has to be considered not only to understand the Raman shifts of QD phonons but also to calculate the strain field in the QDs and their electronic structure.

We have shown that alloying effects are enhanced by the use of higher growth temperatures and by the proximity of neighboring QD layers in stacked QD structures. The Ga content is found to be highest for InAs coverages close to the critical thickness, and decreases as the coverage thickness increases. Our results suggest that the combination of design parameters and growth conditions could be used to control Ga intermixing.

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