

Raman study of atomic intermixing in InAs/AlAs quantum dotsA. Milekhin,^{1,2,*} A. Toropov,¹ A. Kalagin,¹ and D. R. T. Zahn³¹ *Institute of Semiconductor Physics, Novosibirsk, Russia*² *Novosibirsk State University, Novosibirsk, Russia*³ *Semiconductor Physics, Chemnitz University of Technology, Chemnitz, Germany*

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We present a Raman study of self-assembled InAs quantum dots fabricated in an AlAs matrix at different growth temperatures. Raman experiments carried out under resonant and non-resonant conditions allowed us to investigate InAs-like optical phonons localized in the quantum dots. The frequencies of the optical phonons determined from the experiment are compared with those calculated for strained InAlAs quantum dots by taking into account the confinement effect. On the basis of the analysis, the composition of InAs/AlAs quantum dots grown at different temperatures is determined.

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I. INTRODUCTION

Self-assembled semiconductor quantum dots (QDs) having unique electronic, optical, and vibrational properties due to three-dimensional confinement of electrons and phonons are considered as a promising active media for opto-, micro-, and nanoelectronic devices such as light emitting devices [1], photodetectors [2], and memories [3]. The structural parameters of the QDs (size, shape, and areal density of QDs, internal strain and atomic intermixing) are equally important because they govern the QD properties and change electronic and phonon spectra of the QDs. Methods of direct structural analysis such as transmission electron microscopy, atomic force microscopy, and scanning tunneling microscopy are widely used to determine these parameters. However, these methods are commonly destructive, time consuming, and require a special sample preparation. Non-destructive optical methods (in the first place photoluminescence and Raman spectroscopy) provide supplementary valuable information on the structural properties of nanomaterials. Among these, Raman spectroscopy, which is traditionally used for studying vibrational properties of nanostructures [4], allows the determination of internal strain and atomic intermixing in Ge/Si or III-V QDs [5–10]. The most investigated among the self-assembled III-V QDs is the InAs/GaAs system. It was already shown by direct methods [11, 12] and confirmed by optical measurements that Ga atoms are incorporated into QDs forming an InGaAs solid solution [8–10]. An introduction of Al in the GaAs matrix causes unintentional incorporation of Al atoms in InGaAs QDs [10]. A qualitative analysis of optical phonon frequencies obtained from Raman experiments with InAs/AlGaAs QDs shows that Al/In intermixing is weaker than Ga/In intermixing. However, a quantitative estimation of the Al content in QDs of quaternary InAlGaAs solid solution is hardly possible because several effects (such

as strain, phonon confinement, and dispersion of optical phonons in InAlGaAs) should be taken into account. Raman scattering by InAs/AlAs QDs was not investigated despite the fact that the bandgap energy of the latter lies in the visible spectral range making resonant Raman experiments with InAs/AlAs QDs possible.

In our paper, we present a Raman study of the In/Al intermixing in InAs/AlAs QDs, which is based on the preliminary performed Raman analysis of optical phonon dispersion in InAlAs solid solution [13] and which takes into account strain and confinement effects in the QDs.

II. EXPERIMENT

The nanostructures studied were grown by molecular beam epitaxy on (001)-oriented GaAs substrates utilizing Stranski-Krastanov growth mode using a Riber 32P system. The samples are composed of 20 periods of 3 ML InAs deposited on a 20 nm AlAs layer. The substrate temperature was 460, 525, and 535°C during the growth of InAs QDs (samples A, B, and C, respectively). After the deposition of the nominal amount of island material, the growth was interrupted for 10 s (sample A) or 30 s (samples B and C). After the dot formation, the first 10 nm of AlAs spacers were grown at the same temperature as the QDs. The remaining AlAs spacer was deposited at elevated temperature (610°C). The whole structure was covered by 5 nm of GaAs to prevent sample oxidation.

The Raman spectra were recorded at $T = 20$ K using a Dilor XY800 spectrometer. The lines of Ar^+ and Kr^+ lasers were used for excitation. The spectra were measured in backscattering geometry parallel to the growth axis. The scattering configuration employed was $z(y,x)-z$ with x , y , z parallel to the $[100]$, $[010]$, and $[001]$ directions, respectively. The spectral resolution was 2 cm^{-1} over the entire spectral range.

III. DISCUSSION

In order to evaluate the In/Al intermixing in InAs/AlAs QDs, one has to determine the impact of strain and confinement on the frequencies of the optical phonons. Fig. 1 shows the Raman spectra of sample A measured with different excitation energies. One can see that the feature assigned to LO optical phonons localized in InAs/AlAs QDs shifts from 263 to 245 cm^{-1} with an increase in the excitation energy from 1.65 to 2.62 eV, while the frequency position of LO optical phonons from GaAs (295 cm^{-1}) remains unchanged. It was already discussed [14] that the asymmetrical shape of the InAs QD phonon lines in the Raman spectra and its dependence on the excitation energy are caused by QD size distribution and phonon confinement in small-size dots.

In large QDs, phonon confinement effects are negligible and the optical phonon energies are affected by strain only. These QDs have lower energies of electronic interband transitions (below 1.8 eV) [15]. The contribution of these QDs to the Raman spectra is stronger for excitation lines in the red spectral range that are closer to the resonance with

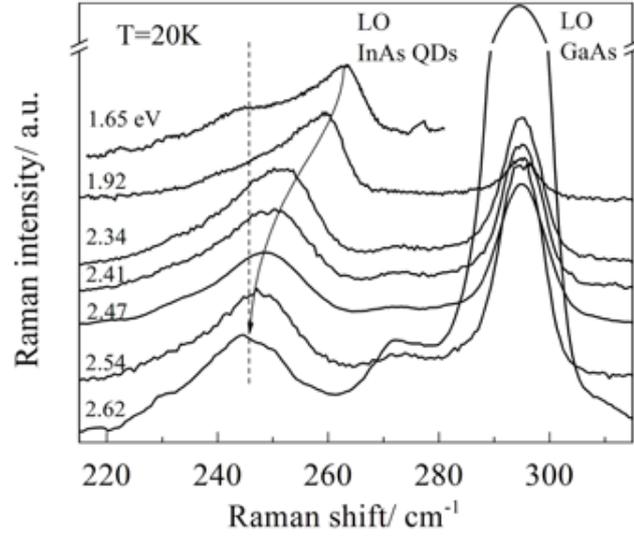


FIG. 1: Raman spectra of sample A measured with different excitation energies.

electronic transitions. Therefore, the position of the LO phonon lines of InAs QDs in the Raman spectra excited with 1.65 eV (258 cm^{-1}) is determined only by the strain distribution, while the influence of the phonon confinement can be neglected. The smaller QDs have higher energies of interband transitions. Therefore, the relative contribution of small dots to the Raman spectra increases at higher excitation energies. In smaller-size dots, the phonon confinement effect becomes more significant and causes a noticeable decrease in the phonon frequencies (Fig. 1).

It is worth to mention, that the resonance conditions for samples with different composition of QDs e.g. grown at different temperatures can be different due to different energies of interband electronic transitions in QDs. As the result, the “resonant” QD size selected by given wavelength in Raman process will be larger for higher temperatures. In this case, the effect of phonon confinement may diminish.

Therefore, one would expect that the analysis of the Raman spectra of InAs/AlAs QDs measured with low excitation energies (e.g. 1.65 eV) can allow the strain and atomic intermixing in the QDs to be evaluated. However, the Raman scattering by the QDs grown at elevated growth temperatures (above 520°C) is very weak. Increasing the growth temperature leads to renormalization of the electronic spectrum of QDs and to either a strong PL signal or withdrawing from Raman resonant conditions, which results in the vanishing Raman response from the QDs. This makes the analysis of the phonon frequencies derived from the Raman spectra of the QD structures excited at low energies hardly possible. Therefore, the Raman spectra (Fig. 2) of the grown QDs were measured using the 488 nm (2.54 eV) laser line and the InAs-like optical phonon frequencies from all three samples (samples A, B, and C) were analyzed by taking into account the confinement-induced frequency shift, which amounts to 15.5 cm^{-1} .

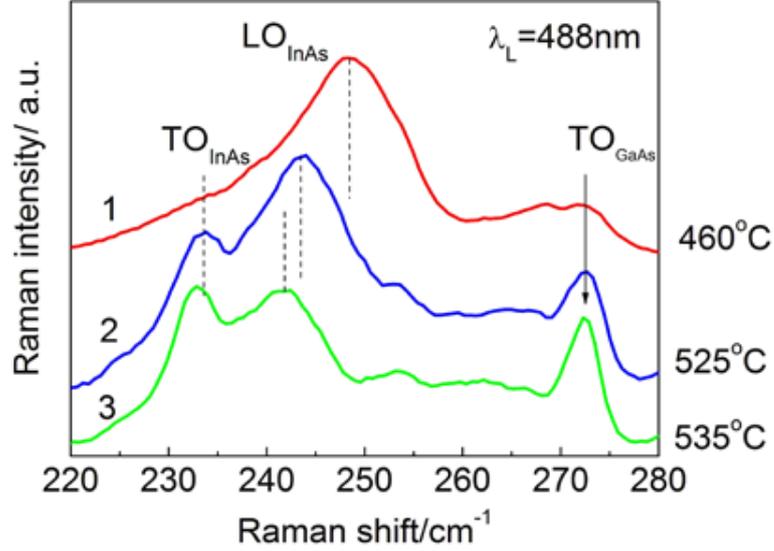


FIG. 2: Raman spectra of samples A, B, and C measured using the 488-nm laser line.

One can see from Fig. 2 that the frequency position of the LO InAs-like phonon in all samples exceeds that of bulk InAs (238 cm^{-1}) and shifts from 248.5 to 241.5 cm^{-1} with an increase in the growth temperature from 460 to 535°C . The peak observed at 272 cm^{-1} refers to TO phonons from GaAs cap layer and substrate.

The first issue is due to the fact that InAs QDs are subject to compressive strain while the second one can be explained by the strain relaxation due to a higher degree of In/Al intermixing in InAlAs QDs grown at elevated temperatures. The same trend but accomplished by a weaker shift is also observed for the TO InAs-like phonons.

According to ref. [16] the shift of LO and TO phonon frequencies induced by biaxial strain in InAs can be written as

$$\Delta\omega_{LO}(x) = \omega_{LO}(x) \cdot \left[K_{11}^{LO} \cdot \frac{\varepsilon_{zz}(x)}{2} + K_{12}^{LO} \cdot \varepsilon_{xx}(x) \right] \quad (1)$$

$$\Delta\omega_{TO}(x) = \omega_{TO}(x) \cdot \left[K_{11}^{TO} \cdot \varepsilon_{xx}(x) + K_{12}^{TO} \cdot (\varepsilon_{xx}(x) + \varepsilon_{zz}(x)) \right] \quad (2)$$

Here $\varepsilon_{zz}(x) = -2 \cdot C_{12}(x) \cdot \frac{\varepsilon_{xx}(x)}{C_{11}(x)}$, where $\varepsilon_{xx}(x)$, $\varepsilon_{yy}(x) = \varepsilon_{yy}(x)$ and the diagonal components of the strain tensor, $\omega_{LO}(x)$ and $\omega_{TO}(x)$ are the composition dependent frequencies of LO and TO InAs-like phonons, $C_{ij}(x)$ is the elastic stiffness for $\text{In}_x\text{Al}_{1-x}\text{As}$ [17], and are phonon deformation potentials for InAs [17]. Note, that the dependences and are taken from [13].

The frequency positions of LO and TO phonons in strained InAlAs QDs as a function of In content calculated according to equations (1) and (2) in comparison with the

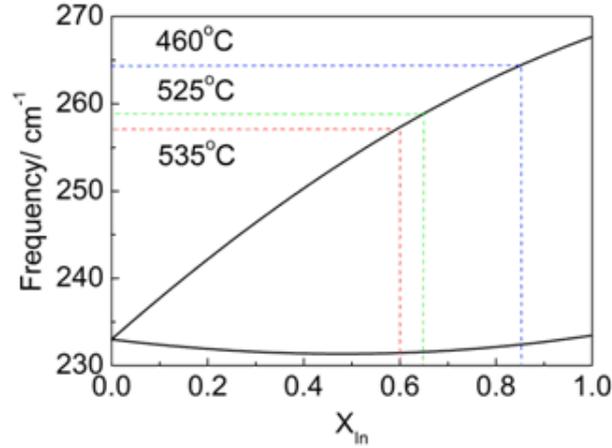


FIG. 3: Calculated frequency positions of LO InAs-like phonons in strained $\text{In}_x\text{Al}_{1-x}\text{As}/\text{AlAs}$ QDs. The frequency positions of the modes observed in the experiment and the corresponding In content are indicated by the dashed lines.

experimental data are presented in Fig. 3. In order to eliminate the influence of the confinement effect on the optical phonons in QDs the experimental phonon frequency positions shown in Fig. 1 are shifted towards higher frequencies by 15.5 cm^{-1} in accordance with the discussion described above. From the comparison of the calculated and experimental phonon frequencies, the In content in InAlAs QDs is found to be 0.85, 0.65, and 0.6 for the samples A, B, and C, respectively. As expected, the increasing growth temperature promotes the effective incorporation of Al atoms from the AlAs layers into the InAs QDs with the formation of mixed InAlAs QDs. The occurrence of In/Al intermixing in similar QDs was evidenced by scanning tunneling microscopy (STM) [12] and photoluminescence [15, 18]. The decrease in the indium concentration from 0.8 to 0.75 from the base towards the top observed in STM experiments for the InAs/AlAs QDs grown at 500°C is in good agreement with our results.

Photoluminescence data indicate that In/Al intermixing in InAs/AlAs QD arrays becomes more effective with increasing growth temperature and growth interruption [15]. The In content for structures similar to samples A, B, and C was also determined by PL and amounts to 0.9, 0.73, and 0.420.73, respectively, which agrees well with our data. A deviation of the results obtained by PL experiments [15] and our data can be due to an increasing size of the QDs with increasing growth temperature, which was not taken into account in our calculation. However, a small intermixing (less than 10%) was estimated from the analysis of phonon replica in the PL spectra of a single InAs/AlAs QD grown at 530°C [18], which reflects the difference in growth conditions for the arrays of QDs.

IV. CONCLUSIONS

In conclusion, we have performed the analysis of InAs-like optical phonon frequencies derived from resonant and non-resonant Raman scattering data of InAs/AlAs QD arrays grown at different temperatures. The variation in the phonon frequency positions with increasing growth temperature indicates an increasing In/Al intermixing in the QDs. We have shown that Raman spectroscopy allows the degree of the intermixing in self-assembled InAs/AlAs to be determined when the confinement effect of optical phonons and the mechanical built-in strain are taken into account.

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