# Self-assembled InAs quantum dots in wide-bandgap matrices of AlAs and aluminum oxide, studied by Raman and infrared spectroscopies

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**Abstract.** We present Raman and infrared studies of phonons in self-assembled multilayer structures with InAs quantum dots (QD's) in AlAs matrix, and the first Raman study of InAs QD's embedded in aluminum oxide. The InAs/AlAs QD structures were grown by molecular beam epitaxy on GaAs (001) substrates. The observed main features of Raman spectra of self-assembled InAs QD's in AlAs matrix include: 1) asymmetric lines of QD LO phonons affected by strain, confinement and size inhomogeneity of QD's; 2) the confined phonons of InAs wetting layer (WL); 3) the two bands of interface phonons in the AlAs frequency region, attributed to phonons associated with two types of interfaces: the planar interface WL/AlAs matrix and the three-dimensional QD/matrix interface; 4) the doublets of folded acoustic phonons caused by periodicity in the multilayer QD structures. The confined TO phonons in the InAs QD's were observed in the infrared spectra. The influence of growth temperature, varied from 420 to 550°C on the morphology of QD's was investigated. QD's grown at 420°C are found to have the smallest size. Increasing the temperature up to 480°C leads to the formation of larger InAs islands and improved size homogeneity. Further temperature elevation (above 500°C) causes partial re-evaporation of InAs leading to a decrease of QD size and density, and, finally, their complete disappearance. InAs QD's embedded in aluminum oxide were fabricated by selective oxidation of AlAs matrix in self-assembled InAs/AlAs QD's. Micro-Raman spectroscopy data show that depending on oxidation conditions (humidity, temperature) InAs QD's in an oxide matrix can be even more strained than before oxidation, or become fully relaxed. At the boundaries of oxidized/non-oxidized areas the presence of amorphous and crystalline As clusters is evident.

## 1. Introduction

Semiconductor quantum dots (QD's) obtained by self-organized growth in highly strained heteroepitaxial systems have been intensively studied during the last years (for a review see e.g. Refs. [1,2]). Recently InAs QD's embedded in wide bandgap matrices of AlAs and AlGaAs have received increasing attention [3-5]. Higher barriers of the AlAs matrix produce shifts of the InAs QD bandgap energy towards the visible range as well as improved temperature stability of light-emitting devices.

Most studies of self-assembled QD's so far have been dealing with their structural and electronic properties. The phonon spectrum of QD's received much less research attention. We present Raman and the first infrared studies of phonons in self-assembled InAs QD's in an AlAs matrix. Our results show both strain and confinement effects on the optical phonon spectra of InAs/AlAs QD's. Also we report the first Raman study of InAs QD's embedded in aluminum oxide, obtained by selective oxidation of AlAs layers in InAs/AlAs QD structures.

## 2. InAs/AlAs QD growth and characterization

We have studied a series of InAs QD's in AlAs matrix grown by molecular beam epitaxy on GaAs (001)-oriented substrates. The samples for Raman studies consist of five layers of InAs QD's separated by 8–12 nm AlAs spacers, while infrared reflectivity (IR) spectra were recorded required on QD structures having 50 periods of InAs QD's.
In the most samples studied the substrate temperature during the QD formation was 460–480°C. However, a series of InAs QD's grown at substrate temperatures varied in the range of 420–550°C was studied by Raman spectroscopy to investigate the influence of the growth temperature on the QD morphology. Special attention was given to the process of capping InAs QD's by AlAs spacer layers. To avoid an In segregation the temperature was kept the same as during the QD growth until the QD's are completely covered by AlAs. Then the growth temperature was elevated to 600°C in order to obtain flat AlAs surface for further growth of the next QD layer.

The growth monitoring by reflection high-energy electron diffraction showed that the transition from a two-dimensional to a three-dimensional growth mode for all the samples occurs after the deposition of 1.8 monolayers of InAs. After the deposition of the nominal amount of InAs (2 to 2.5 monolayers), the growth was interrupted for 100 s allowing self-assembled islands to reach equilibrium sizes.

High-resolution transmission electron microscopy (HRTEM) was used for structural characterization of QD structures. Fig.1 shows a typical TEM image of InAs QD's in AlAs matrix (the QD growth temperature for this sample was 460°C). According to the TEM data, QD's are vertically aligned, have the shape of truncated pyramids. HRTEM shows the InAs QD's to be pseudomorphic, i.e. the structures do not contain misfit dislocations.

Raman spectra were recorded at 80 and 300 K in a backscattering geometry using a Dilor *XY* triple spectrometer equipped with a multichannel CCD detector. Several lines of $Ar^+$ and $Kr^+$ lasers (2.41, 2.18, 1.92, 1.83, and 1.65 eV) were used for excitation. The infrared reflectivity (IR) spectra of QD structures were measured at oblique incidence in the p-polarized light.

## 3. InAs QD's in AlAs matrix

Fig. 2 shows the characteristic Raman spectra of self-assembled InAs QD's in AlAs matrix (for a sample grown at 480°C). The spectra contain the doublet peaks of folded longitudinal acoustic phonons in the low-frequency region (Fig. 2a). The positions of

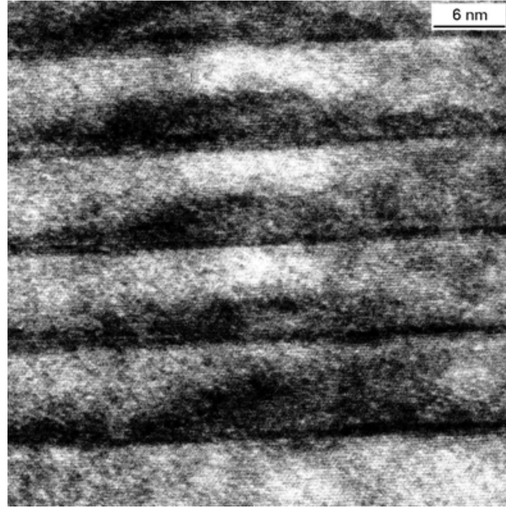


**Figure 1**. Cross-sectional TEM image of InAs QD's embedded in AlAs (QD's were grown at 460°C). Dark and light regions correspond to InAs QDs and AlAs layers, respectively.

the doublets agree well with the values calculated using the elastic continuum model for a superlattice with the same average period (down triangles in the Fig. 2a). Observationof the folded LA phonons in the Raman spectra of multilayer QD structures evidences their good structural quality.

The Raman spectra in the InAs optical phonon region are presented in the Fig. 2b. The LO phonon features of InAs QD's are affected by both strain and confinement. For the large coherently strained InAs QD's in a GaAs matrix, where the confinement effect is negligible, the LO phonon frequency was reported to be 259-260 cm$^{-1}$ [6-8]. This frequency is strongly shifted from the bulk InAs value (242 cm$^{-1}$) due to the large

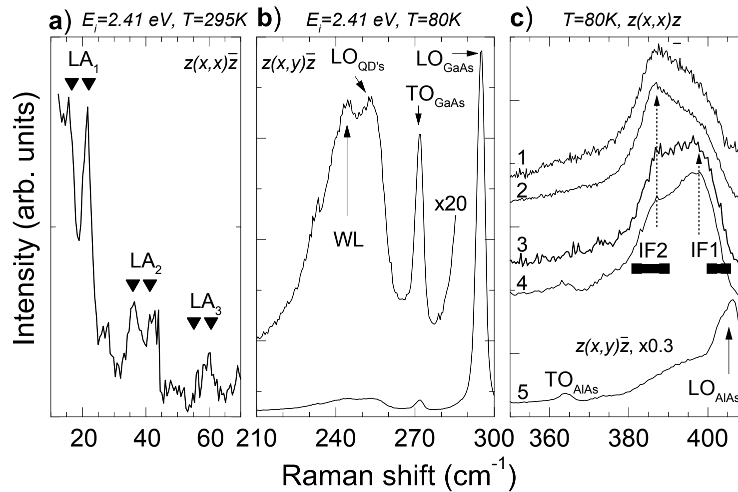


**Figure 2**. Raman spectra of self-assembled InAs QD's in AlAs matrix: **a)** the low frequency region; **b)** the region of InAs and GaAs optical phonons; **c)** polarized Raman spectra in the AlAs optical phonon region, measured with different laser lines: 1.83, 1.92, 2.18, and 2.41 eV (1–4, respectively). The spectrum in crossed polarization geometry, measured with 2.41 eV line (5), is given for comparison.

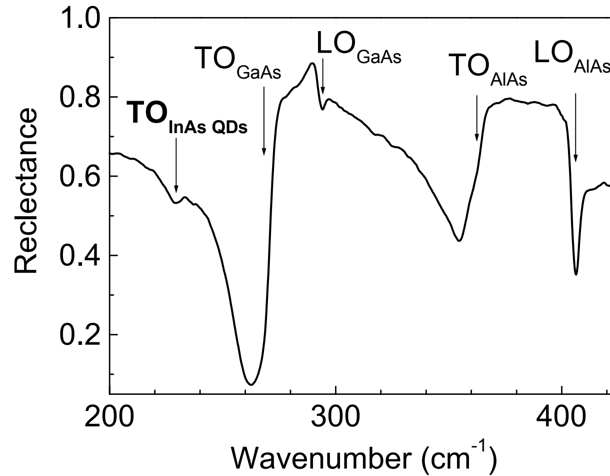


**Figure 3**. IR spectrum of self-assembled InAs QD's in an AlAs matrix, recorded at oblique incidence using *p*-polarized light.

compressive strain. For the InAs/AlAs sample shown on the Fig. 2b the QD LO phonon feature is observed at ~254 cm$^{-1}$. This indicates significant confinement effect, causing the downward shift of the phonon line. The IR spectra of an InAs/AlAs QD structure (Fig. 3) show significant phonon confinement effect, too. The TO phonons of InAs QD's are observed in the IR spectra at ~230 cm$^{-1}$ (28.5 eV), while in InAs/GaAs QD's the TO phonons were reported to have an energy of 30.3 eV [9]. The stronger phonon confinement effect in InAs QD's embedded in AlAs evidences their smaller average size compared to the InAs QD's in a GaAs matrix. This is consistent with the results of *in situ* scanning tunneling microscopy studies of InAs/(Al,Ga)As self-assembled islands [10].

The phonon line of an InAs wetting layer (WL) is seen in the Raman spectra of InAs/AlAs QD structures (Fig. 2b) at 244 cm$^{-1}$. This line was observed also in the Raman spectra of a planar superlattice $(AlAs)_{30}(InAs)_{1.5}$, having an InAs layer thickness just below the threshold of three-dimensional island formation [11]. This confirms its attribution to the WL phonons. This line has a lower frequency than the QD phonons because of the confinement effect in the thin wetting layer.

A common feature of the self-assembled QD structures is island size fluctuation. The size non-uniformity causes the asymmetric Raman line shape of LO phonons in InAs QD's embedded in AlAs and its dependence on excitation energy, reported in our recent paper [11]. Large dots have lower bandgap energies (1.6–1.7 eV for InAs/AlAs QD's [4,5]), and their contribution to Raman spectra increases for excitation lines in red spectral range, which are closer to electronic resonances in large QD's. Therefore, for low excitation energies the observed position of QD phonon lines approaches the values reported for large InAs QD's in GaAs matrix, where the confinement effect is small. Upon increasing excitation energy the relative contribution of smaller dots and wetting layer increases [11], as they have higher energies of electronic transitions. The asymmetric phonon line shape is characteristic of Raman spectra of nanocrystalline structures. It can be described by a model of phonon confinement in nanoclusters of inhomogeneous size [12,13].

Fig. 2c shows the Raman spectra of InAs/AlAs QD structures in the AlAs optical phonon region. Two broad bands labeled by IF1 and IF2 dominate the spectra recorded

in parallel polarization geometry. These bands are attributed to the interface phonons associated with two types of interfaces: the planar interface between WL and AlAs matrix and three-dimensional QD/matrix interface, respectively. Horizontal bars show the interface phonon bands calculated using the dielectric continuum model [14] for a planar superlattice and spherical clusters. The model provides reasonable agreement with experimental spectra. For the planar interface the calculated band is close to the AlAs LO phonon because of the high thickness ratio of AlAs and InAs layers. The experimentally observed IF1 band is slightly shifted to lower frequencies. This is possibly due to the influence of strain, which is large near the planar interface. The phonon band corresponding to WL/AlAs matrix interface (IF1) becomes more intense with increasing excitation energy as the latter approaches the resonance with electronic transitions in the wetting layer.

We have studied the influence of the growth temperature on the vibrational spectra of InAs QD's in AlAs matrix. Fig. 4 shows Raman spectra of a series of InAs QD's grown at temperatures varied in the range 420–550°C. As one can see, the LO phonon line of QD's grown at 420°C has the lowest frequency, i.e. the confinement-induced frequency shift effect is the largest for this sample. This means that QD's grown at 420°C have the smallest average size. Increasing the growth temperature up to 480°C leads to the high-frequency shift of the InAs QD phonon line maximum and the decrease of its line width. This evidences the formation of larger InAs islands and improved size homogeneity. Further increase of the substrate temperature (500°C and higher) leads to the broadening of the QD phonon line, decrease of its frequency and intensity. This is probably due to partial re-evaporation of InAs causing the decrease of QD size and density. In the sample grown at 550°C the evaporation of InAs leads to complete disappearance of the InAs QD's. (The spectrum of this sample is not shown in the Fig. 4, since it has no InAs phonon features at all.)

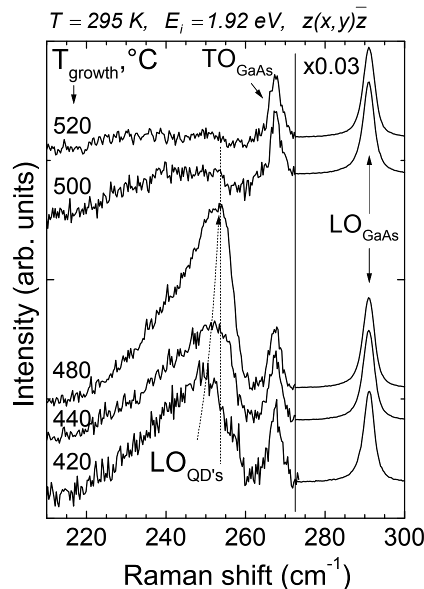


**Figure 4**. Raman spectra of InAs QD's (embedded in AlAs) grown at different substrate temperatures. Dotted lines are guides to the eye.

## 4. InAs QD's embedded in aluminum oxide

We performed the first experiments on synthesis of InAs QD's embedded in Al oxide. The samples were obtained by selective wet oxidation [15] of AlAs matrix in InAs/AlAs QD structures. After the growth of the self-assembled InAs/AlAs QD's the 15 μ mesa-structures were fabricated by a standard photolithography and wet chemical etching. The mesa-structures were oxidized, and the oxidation front was investigated by micro-Raman spectroscopy (the spot size on the sample surface was ≈1 μm) Preliminary Raman results show that depending on oxidation conditions (humidity, temperature) the InAs QD's in an aluminum oxide matrix can become fully relaxed [16] or even more highly strained than original InAs QD's in AlAs matrix before the oxidation.

Fig. 5 shows the micro-Raman spectra for an InAs QD sample after the AlAs oxidation. The spectrum taken from a non-oxidized area contains the LO and TO phonon peaks of AlAs layers, GaAs substrate, and the LO phonon line of InAs QD's. The spectra of an oxidized area show an increase of the InAs QD LO peak intensity and ~5 $cm^{-1}$ shift of the phonon line position towards higher frequency. The first effect is explained by the wider bandgap of the aluminum oxide matrix compared to AlAs leading to a shift of confined electronic states in InAs QD's closer to resonance with the laser excitation energy. The high-frequency shift of the QD phonon line is caused by an increased mechanical strain in the InAs QD's due to shrinkage of the aluminum oxide layers in the oxidation process. At the boundaries of oxidized and non-oxidized areas two features appear in the Raman spectra, evidencing the presence of amorphous and crystalline As clusters. The crystalline As is characterized by the line at 198 $cm^{-1}$, while the broad band centered at ~227 $cm^{-1}$ corresponds to amorphous As [17]. It should be noted that we did not observe the characteristic lines of amorphous $As_2O_3$ at 475 $cm^{-1}$, indicating the absence of this possible product of the oxidation process. These first results demonstrate the formation of InAs QD's in wide bandgap matrix of aluminum oxide. However, optimization of the selective oxidation process is required to form InAs QD's with defined size and strain state as well as homogeneous oxide matrix.

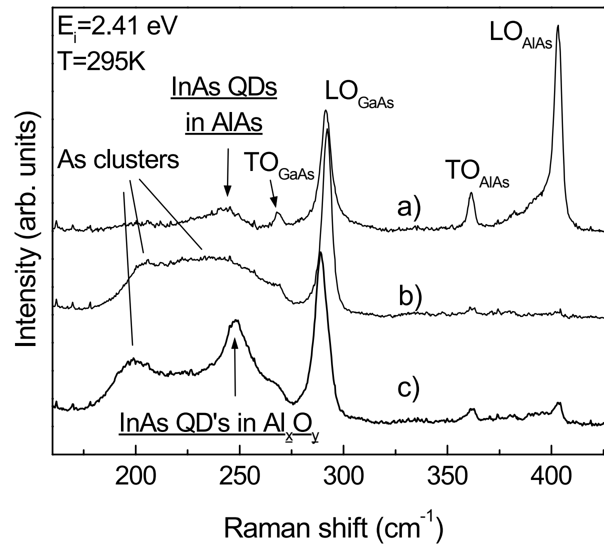


**Figure 5**. Raman spectra of InAs QD's after the oxidation of AlAs layers, taken from a non-oxidized area (a), a boundary of oxidized and non-oxidized areas (b), and an oxidized area (c).

## 5. Summary

We have investigated the vibrational spectra of self-assembled InAs quantum dots embedded in AlAs by Raman and infrared spectroscopy. The observed asymmetric lineshape of LO phonons in the Raman spectra of InAs QD's and its low-frequency shift with increasing excitation energy are explained by QD size distribution and phonon confinement in smaller-size dots. The infrared spectra reveal the features related to the confined TO phonons in the InAs QD's. Confined phonons of the InAs wetting layer (WL) are observed in the Raman spectra of QD structures. Two bands of interface phonons in the Raman spectra in the AlAs frequency region are attributed to phonons associated with two types of interfaces: the planar interface WL/AlAs matrix and the three-dimensional QD/matrix interface. A series of InAs QD's grown at substrate temperatures varied from 420 to 550°C were studied by Raman spectroscopy. We demonstrated that increasing the growth temperature from 420 to 480°C leads to the formation of larger InAs QD's and improved size homogeneity. However, the temperature elevation up to 500°C and above causes partial re-evaporation of InAs leading to decrease of QD size and density, and, finally, their complete disappearance.

InAs QD's embedded in aluminum oxide fabricated by selective oxidation of AlAs matrix in self-assembled InAs/AlAs QD's were studied for the first time. Micro-Raman spectroscopy data allow determining the strain state in InAs QD's in an oxide matrix, which depends strongly on the oxidation conditions. Also, micro-Raman spectroscopy provides evidence of the presence of such AlAs oxidation products as amorphous and crystalline As clusters at the boundary of oxidized/non-oxidized areas.

## 5. Acknowledgements

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