Formation of InAs quantum dots in an aluminium oxide matrix by lateral selective wet oxidation.

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Abstract

Raman spectroscopy which provides valuable information on the structural parameters of QDs was used for monitoring of the lateral oxidation of InAs/AlAs QD structures and study of the phonon properties of InAs QDs in aluminium oxide matrix.

Optical phonons of InAs QD's were found to be affected by both strain and confinement. Raman spectra measured from non-oxidized area reveal asymmetric lineshape of LO phonons in InAs QDs and demonstrate its low-frequency shift with increasing excitation energy that is explained by QD size distribution and phonon confinement in smaller-size dots. Raman spectra taken from oxidized area show an increase of the LO peak intensity and the shift of the phonon line position towards higher frequency. The first effect is explained by formation of wide bandgap aluminium oxide matrix that leads to the shift of confined electronic states in InAs QDs closer to the resonance with the laser excitation energy. The latter is caused by increasing mechanical strain in InAs QDs due to a shrinkage of the aluminium oxide layers. At the boundaries of oxidized/ non-oxidized areas the presence of amorphous and crystalline As clusters is evident.

Introduction.

The technique of lateral selective wet oxidation of Al(Ga)As has been widely used in the fabrication of various optical devices such as photon crystals [1] , light emitting diodes, vertical-cavity quantum dot (QD) lasers [2,3]. Oxidized Al(Ga)As layers are used as a current aperture for achieving both optical and electrical confinements and for formation of Al_xO_y/GaAs distributed Bragg reflector mirrors with a high reflection [4,5] . The application of this process to vertical cavity quantum dot lasers has led to significant performance improvement.

At present, the process of the lateral selective wet oxidation of the Al(Ga)As layers in the GaAs/Al(Ga)As structure is intensively studied [6,7]. The influence of many parameters (oxidation temperature, Al content x in $Al_xGa_{1-x}As$ layers, layer thickness, geometry of the mesa structure) on the wet oxidation kinetics was investigated [8,9].

In this paper we report on using the technique of the selective wet oxidation for the formation of InAs quantum dots in an Al_xO_y matrix with the purpose of application of this structure as an active media of vertical cavity QD lasers.

Experiment.

A series of samples with InAs QDs in an AlAs matrix were grown by molecular beam epitaxy on GaAs (001)-oriented substrates. The samples studied consist of five (sample A) or ten (sample B) layers of self-assembled InAs QDs. The spacer thicknesses are 8 nm for sample A and 30 nm for sample B. After growing 10 nm of AlAs at 580°C the substrate temperature was decreased to 420°C and InAs was deposited with the growth rate of about 0.1 monolayers (ML)/s. The amount of the deposited InAs was equal to 2 MLs for both samples. The deposition of AlAs layers was made in two steps. The first 4 nm of AlAs spacer layer was grown at the same temperature as for InAs layer, then the temperature of the substrate was increased and growth of AlA layers was continued. The growth was monitored by reflection high-energy electron diffraction (RHEED). According to RHEED data, the transition from a two-dimensional to three-dimensional

growth mode (beginning island formation) occurs after deposition of 18 MLs of InAs. The whole structure was capped by 20nm of GaAs layer.

The InAs QDs embedded in aluminium oxide were fabricated by self-organized growth of InAs QDs in AlAs matrix and subsequent selective oxidation of AlAs layers. The lateral oxidation of the AlAs layers was performed in a horizontal quartz tube at 360°C with N_2 as a carrier gas passing through a H_2O bubbler operating at 95°C. The carrier gas fed into the bubbler was regulated at 0.3÷1 liters/min. A typical lateral oxidation depth is 10 μ, the oxidation time is 30 minutes.

The Raman spectra were recorded at 300 K in the backscattering geometry using a Dilor XY triple spectrometer in micro-Raman configuration. The 514.5 nm line of an Ar^+ laser was used for excitation. For study of the oxidation region an microscope was employed to focus the light to the 1 μ spot on the sample.

A structural characterisation of the samples was carried out by cross-sectional high-resolution transmission electron microscopy (HRTEM) using a transmission electron microscope CM20 FEG Philips with Gatan imaging filter GIF 200.

Results.

Figure 1 shows a cross-sectional HRTEM image of as-prepared sample. The light and dark areas correspond to AlAs and InAs QD layers, respectively. According to HRTEM image, the InAs QDs are vertically aligned truncated pyramids with the average base of 11 nm and the height of 2 nm.

Fig. 1. HRTEM image of the sample A

Figure 2 shows low-temperature PL spectra for InAs/ AlAs QDs (sample A). The PL peak at 720nm (1.7 eV) with a full width at half maximum (FWHM) of 60 meV is due to the transition from the first electron excited states to the ground hole state in InAs QDs.

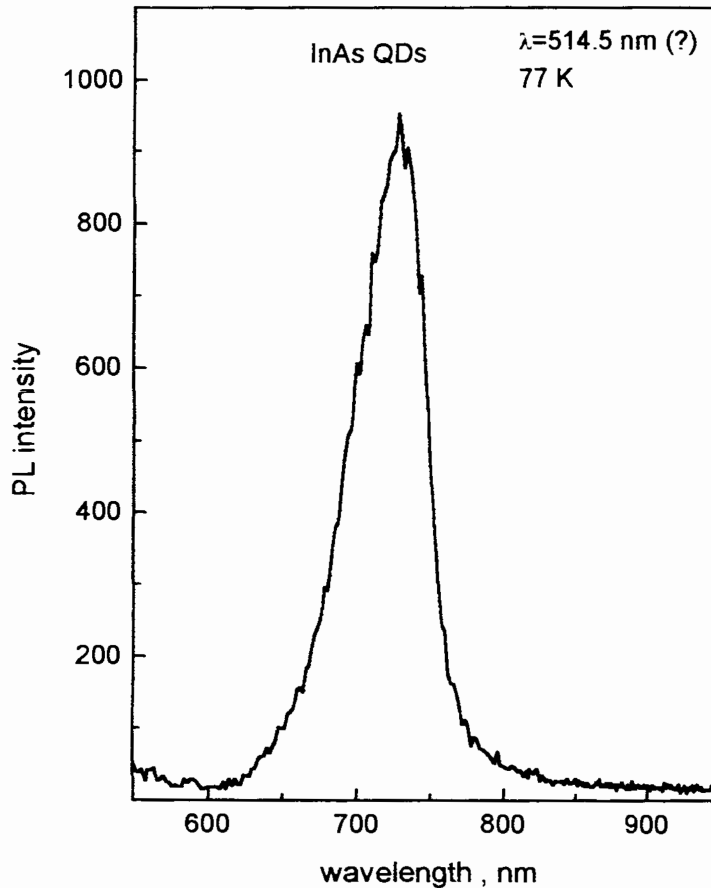
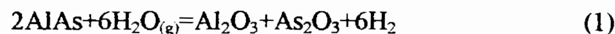


Fig.2. PL spectrum of the sample A taken at 77K
using 514.4 nm laser line of Ar+ laser.

Fgure 3(a) shows the lateral oxidation depth as function of the oxidation time for sample A 120 nm AlAs layers in the temperature range from 360°C to 420°C. The obtained curves are well described by model for Al oxidation proposed in the work [10]. At the initial stage the oxidation depth depends linearly on the oxidation time, since the process of wet lateral oxidation is mostly determined by oxidation reaction. The transport of reagents for further oxidation is presumable realized through the pores in the already formed oxide. Oxidation continues as long as the existing pores allow further penetration of water molecules or oxygen ions. With increasing the oxidation time the pores are blocked by reaction products, that makes difficult the delivery (transport) of reagents and the reaction rate decreases or vanishes.

Fig.3 (a) Lateral oxidation depth w as function of oxidation time time for sample A 120 nm AlAs layers;
(b) Arrhenius plot of the initial oxide growth rate g_0 and the final depth w.

Figure 3(b) shows the dependence of the initial oxide growth rate and the final depth on the oxidation temperature in Arrhenius coordinates. On the basis of the obtained results and the model considered in work[10] the activation energies were calculated for the reactive process at the AlAs/ oxide interface and for the diffusion through the already oxidized material correspondingly $E_1=(1.30\pm0.05)$ eV and $E_2=(0.94\pm0.01)$ eV. The oxidation process is described by the following reactions [11]:



$$2AlAs+6H_2O_{(g)}=Al_2O_3+As_2O_3+6H_2 \qquad (1)$$

$$As_2O_3+3H_2=2As+3H_2O_{(g)} \qquad (2)$$

Both As_2O_3 and As are present as intermediates in the wet oxidation process. Their presence is confirmed by Raman spectra.

Figure 4 shows a cross-sectional HRTEM image of oxidized InAs QD . The light and dark areas correspond to amorphous AlO and crystalline InAs QD , respectively.

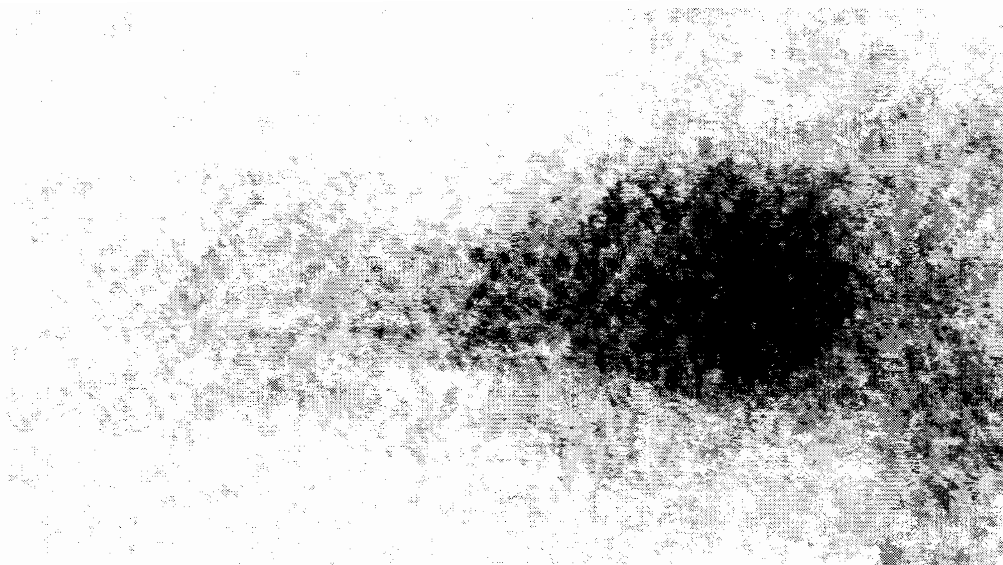


Fig.4 The InAs QD in oxidized matrix

Fig.5a shows the Raman spectra of as-prepared sample B, oxidized sample B and the spectra taken from the border of oxidized/non-oxidized areas. The Raman spectrum of as-prepared sample reveals a number of features attributed to LO phonons in InAs QDs (242 cm-1), TO and LO phonons in AlAs (360 and 402 cm^{-1}) and GaAs (268 and 291 cm^{-1}) and crystalline As clusters (200 cm^{-1}). The frequencies of LO and TO phonons in bulk InAs are 238.6 и 217 cm^{-1}, respectively. The observed frequency position of LO phonons in InAs QDs exceed the corresponding values in bulk InAs. Two reasons can cause the shift of optical phonons- mechanical strain in InAs due to lattice mismatch in InAs and AlAs and confinement

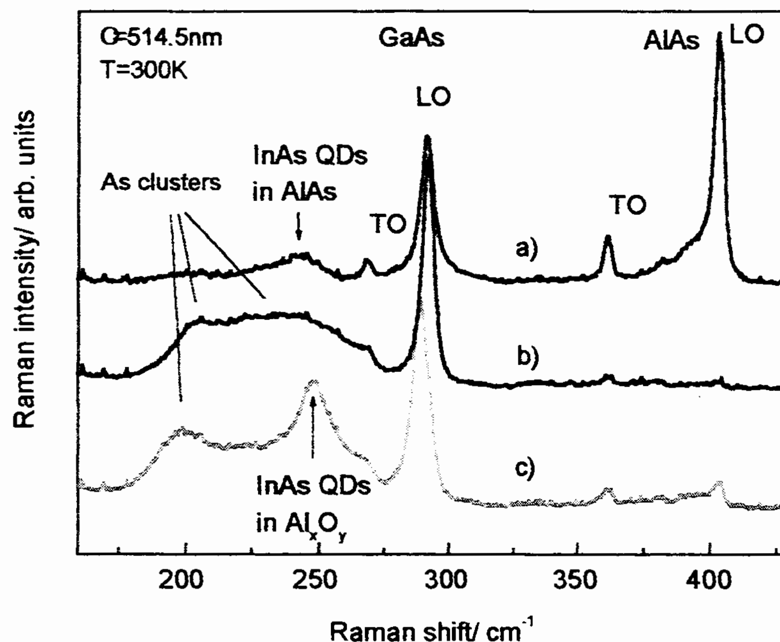


Fig 5. Raman spectra of the sample A taken from non-oxidized area (a), the border of oxidized/non-oxidized areas (b) and oxidized area (c).

effect of optical phonons. The frequency position of experimental optical phonon lines indicate that the investigated nanostructures are pseudomorphic and do not contain dislocations causing strain relaxation. The latter was confirmed by HRTEM experiments. The build-in strain leads to the shift of optical phonon lines towards higher frequency [12]. On the contrary, confinement of optical phonons in the QDs causes the low-frequency shift of LO and TO phonons [13].

Raman spectra measured from the border of oxidized/non-oxidized area (Fig.5b) show decreasing intensity of optical phonons from AlAs spacer, increasing intensity of the phonon line due to crystalline As clusters and appearance of a broad feature centred near 220 cm^{-1} corresponding to amorphous As clusters. The most probable that the intensive signal from the amorphous cluster prevents observation of InAs QD phonons. Raman spectrum taken from oxidized area (Fig.5c) reveals a very pronounced feature at 248 cm^{-1} attributed to LO phonons from highly strained InAs QDs in an aluminuim oxide matrix. Oxidation of AlAs spacer layers causes a shrinkage of the aluminium oxide formed and the further increasing mechanical strain in InAs QDs. It is worth to mention that the experimental conditions of oxidation of AlAs layers (temperature, humidity, flow rate etc.) determine the strain state of InAs QDs in Al_xO_y and can even lead to formation of the fully relaxed InAs QDs [14].

In conclusion, selective oxidation of AlAs layers was used to form InAs QDs in an aluminium oxide matrix. Micro-Raman monitoring of oxidation of the nanostructures evidences the formation of highly strained InAs QDs in Al_xO_y layers and appearance of crystalline and amorphous clusters.

Acknowledgement

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