# Investigation of the buried InAs/GaAs Quantum Dots by Atomic Force Microscopy combined with selective chemical etching

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The subject of the present paper is application of selective chemical etching to investigation of the morphology of the InAs quantum dots (QDs) built in GaAs matrix. Tracing the evolution of the surface morphology and of the optical and photoelectric properties of the QD structures during the etching process allows to determine the actual morphology of the QDs. It was shown that the sizes, shape, and photoelectronic properties of the QDs, grown by Atmospheric Pressure Metal Organic Vapor Phase Epitaxy directly on the surface and the ones of the QDs after removing of the cladding layer are different, that can be explained by differences in the QDs' formation conditions after deposition of InAs layer.

#### Introduction

Scanning probe microscopy (SPM) is used widely for investigation of morphology of the self-organized *InAs/GaAs* quantum dots (QDs). However, for these studies only the QDs located directly on the surface of a structure are suitable, whereas in the electronic devices they are built in a matrix of other wider gap material. Overgrowth of the InAs QDs by a *GaAs* cladding layer can introduce essential changes in the chemical composition, size distribution, and the surface density of the QDs, because formation of the QD layer continues some time after stopping deposition of this layer [1].

In this connection development of the technique for investigation of the buried QD (BQD) layers by SPM is important. In [2] selective chemical etching was used for uncovering the interface of (In,Ga)As/InP heterostructures and investigation of their morphology by Atomic force Microscopy (AFM). In [3,4] we employed the same method for investigation of InAs/GaAs QDs covered by a thin GaAs cladding layer. Here we present the further developments of this method.

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## Experiment

The *InAs/GaAs* QD heterostructures were grown by Atmospheric Pressure Metal Organic Vapour Phase Epitaxy (AP-MOVPE) on semi-insulating GaAs (100), misoriented by 3° towards [110]. The technique of the *InAs* layer deposition and of *Bi* doping of the QD layer during growth for increasing the QDs' uniformity was described in [3,4]. The structures with ~15 nm *GaAs* cladding layer and without this one were grown. The morphology of the QD layers was investigated by Atomic Force Microscopy (AFM) using TopoMetrix<sup>®</sup> Accurex<sup>TM</sup> TMX-2100 AFM in contact mode. Photoluminescence (PL) and photovoltage spectra in the semiconductor/electrolyte barrier (PSE) were measured using the technique described in [4,5].

The *GaAs* cladding layer was etched in the  $NH_4OH:H_2O_2$ :glycol (1:1:30) solution [6], having the etching rate for *GaAs* ~60 nm/min (E1), and in the solution of 0.8M  $K_3[Fe(CN)_6]$  in 0.3M *KOH*): $H_2O$ :glycerine (1:5:2), having the etching rate for *GaAs* ~40 nm/min (E2).

### **Results and Discussion**

The evolution of the morphology of an *InAs/GaAs* QD structure with 15 nm cladding layer etched in the E1 solution is shown in Fig. 1. The nominal etching depth was calculated for thick homogeneous *GaAs* layer etching rate. Apparently, this value is a rough estimation. Comparison of this value with cladding layer thickness allows to determine the etching stop moment at the surface with the increased In concentration. In the investigated QD structures grown by AP-MOVPE the *InAs/GaAs* heterointerface was not sharp as a result of diffusion intermixing of In and Ga at the growth temperature > 500°C. Assumption of a transition  $In_xGa_{1-x}As$  alloy layer at the QDs interface has been made in [3,4] in order to explain some morphology features and photoelectronic properties of the QDs (large sizes of the QDs and low value of the ground transition energy in them). Evidently, after removing of cladding layer by selective etching the surface of the QDs layer have to reveal. This surface will correspond to some threshold value of *x*=const when the etching process has stopped or the etching rate has decreased. Unfortunately, this threshold value of x for used etchants is not known.

Before etching the surface roughness was less than 2 nm (Fig. 1a). At the first stage of etching (up to the nominal depth  $\approx 15$  nm, approximately equal to the cladding layer thickness) the etching process is very inhomogeneous (Fig. 1b): all the etched surface was covered by islands with lateral size 40-50 nm and height  $\sim 10$  nm uniformly and densely, which could be considered to be the QDs mistakenly.

At the etching depth  $\approx 30$  nm the surface topography changes essentially and remains the same until the estimated etching depth reaches 50 nm (Fig. 1c,d). The uniform islands with lateral size  $\sim 40$  nm and surface density  $\sim (0.5-1) \times 10^{10}$  cm<sup>-2</sup> was observed which are the InAs QDs (ESQDs). They are separated from each other by a nearly smooth surface. Apparently, at this stage the GaAs cladding layer was etched completely, and the etching process has been almost stopped by the InAs wetting layer. AFM image of the surface QDs (SQDs) without cladding layer have the similar shape (Fig.1f).

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Fig. 1. Evolution of AFM images of *InAs/GaAs* BQD during etching. The estimated etching depth, nm: a – 0, b – 12, c – 30, d – 42, e – 60. f – AFM image of SQD layer.

If the etching process continues further, the surface becomes similar to the one at the first stage of etching again already at the etching depth  $\sim$ 60 nm (Fig.1e). Thus, there is a rather clearly determined stage of the etching process at which the QDs can be detected authentically.

The other facts confirming that we have observed the QDs actually are:

1. The geometrical parameters of the observed clusters (namely lateral size, height and density) do not differ much from the ones of the SQDs grown at the same conditions.

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Also, the surface density of these QDs is in good agreement with the one determined from the PSE spectra [4].

2. At the second stage of etching the red shift of the ESQDs' PL spectra has been observed (Fig. 2, curve 2) towards the energies that are usual for the SQDs (curve 3). This result can be explained by relaxation of the elastic strain in the QDs when removing the cladding layer [7].

However, the parameters of the BQDs determined by selective chemical etching and the ones of the SQDs grown at the same conditions have some typical differences. The density of the BQDs is 2–3 times higher than the one of the SQDs that can be explained by suppression of coalescence of the nanoclusters by overgrowth by the cladding layer. The SQDs are little higher and have higher aspect ratio.





The presence of the transitional  $In_xGa_{1-x}As$  alloy layer at the QDs/matrix interface should increase the size (especially the base of the clusters) and the effective volume of the ESQDs compared with the ones of SQDs.

Another difference between the SQDs and ESQDs is the difference in the value of the red shift of the QD ground state transition energy relative to the one in the BQDs (Fig. 2, curves 1 and 2). The red shift in the SQDs is usually explained by relaxation of the



Fig. 3. PL (1-3) and PSE (4-6) spectra of the heterostructures. 2-4 – BQDs; 1, 5 – SQDs; 6 – GaAs. 2,4-6 – 300 K; 1, 3 – 77 K.

elastic strain due to absence of the cladding layer. Here we should take into account also the difference in sizes, shape, and the profile of the potential well in the QDs which are in turn affected by distribution of In molar fraction x near the interface.

The E1 etchant was very unstable: the etching rate decreases 2 times per day. In this connection E2 solution, more stable and having good selective properties was explored. Using E2 we have carried out an experiment on tracing the process of removing



the cladding layer by the photovoltage spectroscopy in the QD structure/electrolyte barrier. 0.5M *KCl*:glycerine (1:1) solution was used as the electrolyte.

In the structures with a thin cladding layer part of the clusters was not covered completely. AFM image of the surface of these structures (Fig. 1g) is almost the same to the one of a QD layer with a thick cladding layer (Fig. 1a), the tops of the clusters seen above the cladding layer were diffused only. The surface density of these clusters is  $3 \cdot 10^9 \text{ cm}^{-2}$ . In the PSE spectrum of this structure the SQD photosensitivity bands, with threshold near 0.65 eV and the ones from the BODs with a peak at  $\sim 0.985$  eV were observed (Fig. 3, curve 1). The QDs were observed quite clearly after removing the cladding layer by E2 selective etchant (Fig. 1h). They have the parameters, typical for QDs: the surface density  $\sim 2 \cdot 10^{10}$  cm<sup>-2</sup>, the lateral sizes  $\sim 50$  nm, the height increased up to 5 nm in the process of etching. The corresponding red shift of the QD ground state transition peak (curves 2–4) takes place when removing the cladding layer. Evidently, it is connected with decreasing of the cladding layer thickness and consequently with partial relaxation of the elastic strain in the QDs. Broadening of the peak also takes place. In this experiment stopping the of etching process at the surface with increased In molar fraction was revealed: as the PSE spectrum from the ESQDs was observed after 80 min of etching, for the homogeneous GaAs the etching depth exceeded the cladding layer thickness 20 times at the same etching time.

The maximum value of the red shift of the PSE peak at the BQD to ESQD transformation was  $\approx 90$  meV. This value is close to the one obtained using E1, with control of the etching process by PL and less than the one for the SQDs. This result confirms the conclusion, that the differences in sizes, in shape, and probably in distribution of the chemical composition near the interface which determines the potential well shape, contribute most to the differences in the value of the red shift between the SQDs and the ESQDs.

It is interesting, that during etching the SQDs the photosensitivity threshold shifted to higher energies. Rather small value of this shift indicates that essential etching of SQDs didn't occur. Therefore, size and shape of ESQDs are not high different from one of BQDs, and effect of red shift of ground state transition energy, observed at the removing of cladding layer is dependent from relaxation of elastic strains only.

# Conclusions

Selective chemical etching is a powerful tool for investigation of the morphology of the QDs built in a wider gap semiconductor matrix. However, instability of the etching process, which can result in development of the surface on one hand, and finite selectivity of the etchant on the other hand, require additional information in order to obtain reliable results. Tracing the evolution of the surface morphology and of the optical and photoelectric properties of the QD structures during the etching process allows to determine the moment when the cladding layer is removed completely, and the etching front represent the actual morphology of the QD layer. By this method, it was shown that the sizes, the shape, and the photoelectronic properties of the surface QDs grown by AP-MOVPE and

the ones of the buried QDs after removing the cladding layer are different, that can be explained by differences in the QDs' formation conditions after deposition of InAs layer.

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