# THE LIQUID PHASE EPITAXY OF SELF–ASSEMBLED InAsSbP–BASED STRAIN INDUCED ISLANDS ON InAs SUBSTRATES AND THEIR EVOLUTION FROM PYRAMIDS TO QUANTUM DOTS

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## Abstract

The Liquid Phase Epitaxy technique has been applied for the formation on InAs (100) substrates self-assembled InAsSbP-based strain induced islands. The evaluation of these objects from pyramids to globe and quantum dots (QD) was detected and investigated. The Scanning Electron Microscope (SEM-EDAX – FEI Nova 600–Dual Beam) and Atomic Force Microscope (AFM – TM Microscopes–Autoprobe CP) equipments were used for the investigation of morphology, dimensions (size and shape), distribution density and composition of islands. The EDAX measurements on the top and bottom's angles of InAsSbP quaternary pyramids as well as the lattice mismatch ratio calculations have been carried out. The compositions of quaternary $InAs_{1-x-y}Sb_xP_y$ pyramids with the values of x < 4 at.% and y < 2 at.% were measured. The good symmetry of compositions and lattice mismatch ratio values in the both angles of cut pyramid's base has been detected. Investigations shown, that the strength on the top of pyramids was less than on the bottom's angles and that the size of islands becomes smaller when the lattice mismatch decreases. The average density of the QDs was equal (5-7) $\times 10^9$ $cm^{-2}$, with dimensions of 0, 7-12 nm in height and 20-80 nm in width. The Gaussian distribution of QD's amount versus to their average diameter has been also detected. The critical size ($L_{Critical}$ ~ 500 nm) of InAsSbP-based strain induced pyramid's shape transformation to globe was determined.

## Introduction

In recent years, much research effort has been focused on quantum dots (QDs) and wires [1–3] due to their modified density of states, fascinating optoelectronic properties and device applications in areas such as lasers, photodetectors and electronic devices. From the viewpoint of electronic device application, it is valuable to fabricate QD devices basing on the processing techniques which are compatible with the very large-scale integrated circuit. Among quantum dot and wire fabricating techniques, self-organized Stranski - Krastanov method [4] is an important one by which dislocation-free dots, elongated islands and wires can be produced. By this method, when the islands are in minimum size, quantum dots are circular. Indeed, above a certain critical thickness, the growth mode switches from the conventional layer-by-layer (i.e. two-dimensional, 2D) to a 3D growth mode due to the accumulation of elastic energy in the strained layer that, first, partially relaxes by spontaneously nucleating small islands of strained material and, later, by creating misfit dislocations. These self assembled islands are so small (5–30 nm wide and 0.6–8 nm high, depending on the material and growth conditions) and homogeneous (the size distribution has a broadening of the order of 15%) that they exhibit a strong 3D confinement and behave as QDs. For fundamental physics, some phenomena such as the interaction between coupled dots [5] and the resolution of the quantum states in current–voltage characteristics [6] have been also observed. For optoelectronic devices, it is critical to prepare ordering and uniform QDs. So far, various attempts have been undertaken to improve size and site uniformity for self-organized quantum dots [7–9]. In general, quantum dots have better optical properties than other quantum nanostructures since electrons and holes are trapped in all three dimensions. This leads to a δ – like electronic density of states where the energy levels are totally quantized, which allows for better device performance, such as higher gain and lower threshold currents, less temperature sensitive threshold current and emission wavelength and longer wavelengths to mid-infrared region in laser structures. To increase the responsivity and operating temperature of infrared photodetectors, the efficiency of PV solar cells [10] as well. However, in practice the range of emission and absorption wavelengths is somewhat limited as there is a limited set of material systems that will allow self-assembled quantum dot formation.

The narrow gap III–V semiconductor materials InAs, GaSb, InSb and their alloys are particularly interesting and useful materials since they offer the promise of being able to access the mid– and far infrared wavelength region and should provide the next generation of LEDs, lasers and photodetectors for applications such as infrared gas sensors, molecular spectroscopy, thermal imaging and thermophotovoltaic cells (TPV) [11]. For mid-IR applications (2–10 μm), QDs are normally formed with binary compounds InAs and InSb or InAsSb, InGaAs, InAlAs, InAsP, InAsSbP etc. alloys. InP, GaAs, GaSb and InAs are used as the substrates for forming QDs for mid-IR applications. InAlAs [18], InGaAs [19], InAsP [20], InAsSb [14, 16, 21, and 22], InAsSbP [13], InSb [12, 23] and InAs [14, 24, and 25] QDs for mid-IR emission and Si-Ge [17] islands formation have been investigated. Photoluminescence and electroluminescence emission properties have been investigated and reported for the most narrow band-gap binary and ternary self-assembled quantum dot systems. But for most of the QDs, the emission wavelength is limited around 2 μm. The longest emission wavelength of QDs received comes from InAsSb QDs grown on InAs substrate by improved LPE technique [14]. The emission wavelength reaches 4.29 μm. The peak emission of the QDs was from inter-band transitions in type II band alignment of the InAsSb/InAs QDs. The emission began to quench when the temperature rose above 100 K due to shallow InAs barrier.

It is generally accepted that LPE, which is an equilibrium growth technique, produces epitaxial material of the highest crystalline perfection containing few point defects and impurities and is therefore well suited to the fabrication of optoelectronic devices. However, it is thought to be unsuitable for the growth of quantum wells and quantum dots. The main arguments against conventional LPE relate to the high initial growth rate which results in poor thickness control and reproducibility for thin layer epitaxy. However, it is also possible to use LPE to grow multilayer III–V structures which exhibit quantum size effects [26] and with appropriate modifications LPE has been successfully employed to grow quantum well heterostructure lasers [27, 28]. We also note that it is possible to grow chemically abrupt interfaces by LPE and that quantum wells as thin as 20 Å have been successfully prepared [29]. In [30] the first InAs quantum wells with thickness as low as 25 Å grown by LPE using a special rapid slider technique have reported.

In this paper we report our first efforts for the growth of InAsSbP quaternary self assembled strain induced islands and quantum dots on InAs (100) substrates by liquid phase epitaxy (LPE).

## Experimental procedures

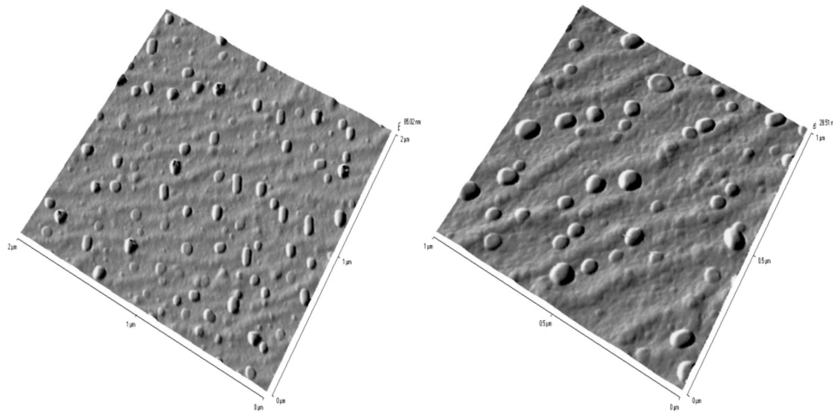
The samples were grown by liquid phase epitaxy (LPE) using a slide-boat crucible. In contrast to other growth techniques as molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD) LPE operates comparatively closer to thermodynamically equilibrium. Consequently, LPE grown islands on (100) oriented substrates exhibit a similar shape for an extended concentration range which consists mainly of truncated pyramids with {111} side facets and an {100} top facet with a nearly constant aspect ratio of island base along (110) to island height of two. To ensure a high purity of the epitaxial layers the entire growth process has performed under a pure hydrogen atmosphere. The InAs substrates used in this work were 11 mm in diameter, (100) oriented, undoped, having background electron concentration of $2\times10^{16}$ $cm^{-3}$. The quaternary alloy $InAs_{0,742}Sb_{0,08}P_{0,178}$ which were used in this work as a base material is conveniently lattice-matched to InAs. We have previously used this alloy for the fabrication of thermophotovoltaic (TPV) cells and mid-infrared diode heterostructures [11].

But in order to expect the formation of strain-induced islands and quantum dots the undersaturated by arsenic and supersaturated by antimony liquid phase have been used. The mole fractions $X_{lAs} = 0{,}0195$, $X_{lSb} = 0{,}1228$ and $X_{lP} = 1{,}7\times10^{-4}$ in the growth melt were used to provide the lattice mismatch between InAs substrate and InAsSbP epilayer up to 2%. The LPE growth solution components – undoped InAs, undoped InP and Sb (6N) are solved in a In (7N)-solution which has been homogenized at first one hour at T=580$^{o}$C then three hours at LPE initial growth temperature of T=550$^{o}$C to equilibrate the system thermodynamically. After that the quaternary liquid phase is brought into contact with the InAs substrate. In order to initialize the growth of islands and quantum dots an over saturation was established by decreasing of initial growth temperature up to 2$^{o}$C using the slower ramp rate.

**Results and discussion**

Atomic force microscopy (AFM) was employed to investigate the resulting morphology and to obtain the size, shape and density of the quantum dots. The used AFM was a TM Microscopes – Autoprobe CP. The images were acquired at a constant scanning force using a silicon nitride soft cantilever probe with a pyramidal tip. In order to ensure that no instrumental artefacts were present in the recorded data, each of the areas of the samples investigated were scanned several times in different directions. In Fig.1 the AFM images of InAsSbP QD's grown by liquid phase epitaxy on InAs (100) substrate from the surfaces of S=2×2 μm$^2$ and S=1×1 μm$^2$ are presented. The InAsSbP quantum dots are clearly visible. Our investigations shown, that the QDs are quite uniformly distributed over the substrate surface. The average density of the QDs was equal (5-7) ×10$^9$ cm$^{-2}$ with dimensions of 0, 7-12 nm in height and 20-80 nm in width. Because the enough large difference in lattice parameter has been provided we consider the growth process to be consistent with the Stranski–Krastanov [4] mechanism, but are unable to confirm the presence of a wetting layer without transmission electron microscopy (TEM) analysis.

The Gaussian distribution of the QDs amount versus their average diameter calculated from the substrate surface S = 4 μm$^2$ was detected (Fig.2). The optimum size of QDs was equal ~ 50 nm.



**a** **b**

**Fig. 1.** The oblique view of AFM images of InAsSbP QDs grown by liquid phase epitaxy on InAs (100) substrate, a – S=2×2 $\mu m^2$, b – S=1×1 $\mu m^2$.

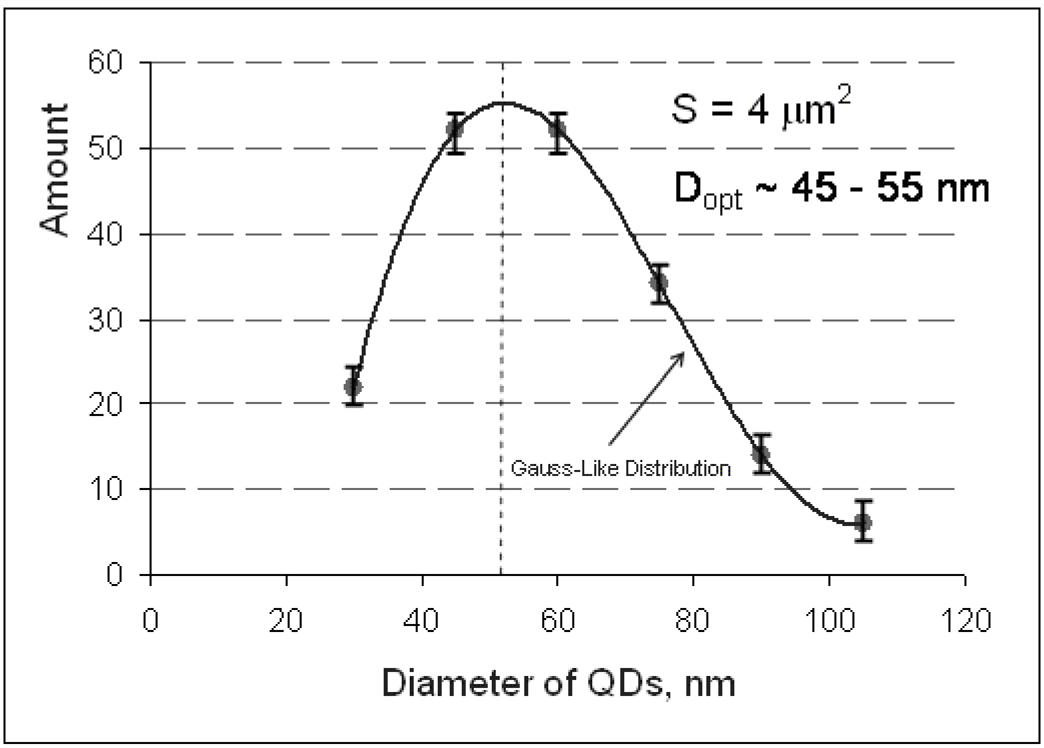



**Fig. 2.** Dependence of the InAsSbP QDs amount versus their average diameter.

During the investigation of grown sample on the substrate surface place to place the strain-induced InAsSbP-based islands mainly in the form of pyramids have been detected. Probably, these islands have formed due to the not sufficient homogenization of growth melt. From our point of view more long time homogenization of liquid phase will prevent the formation of these islands.

The islands in the form of truncated pyramids, pyramids, ellipsoidal and globe-shape surfaces have been detected (Fig.3 a,b,c,d,e).

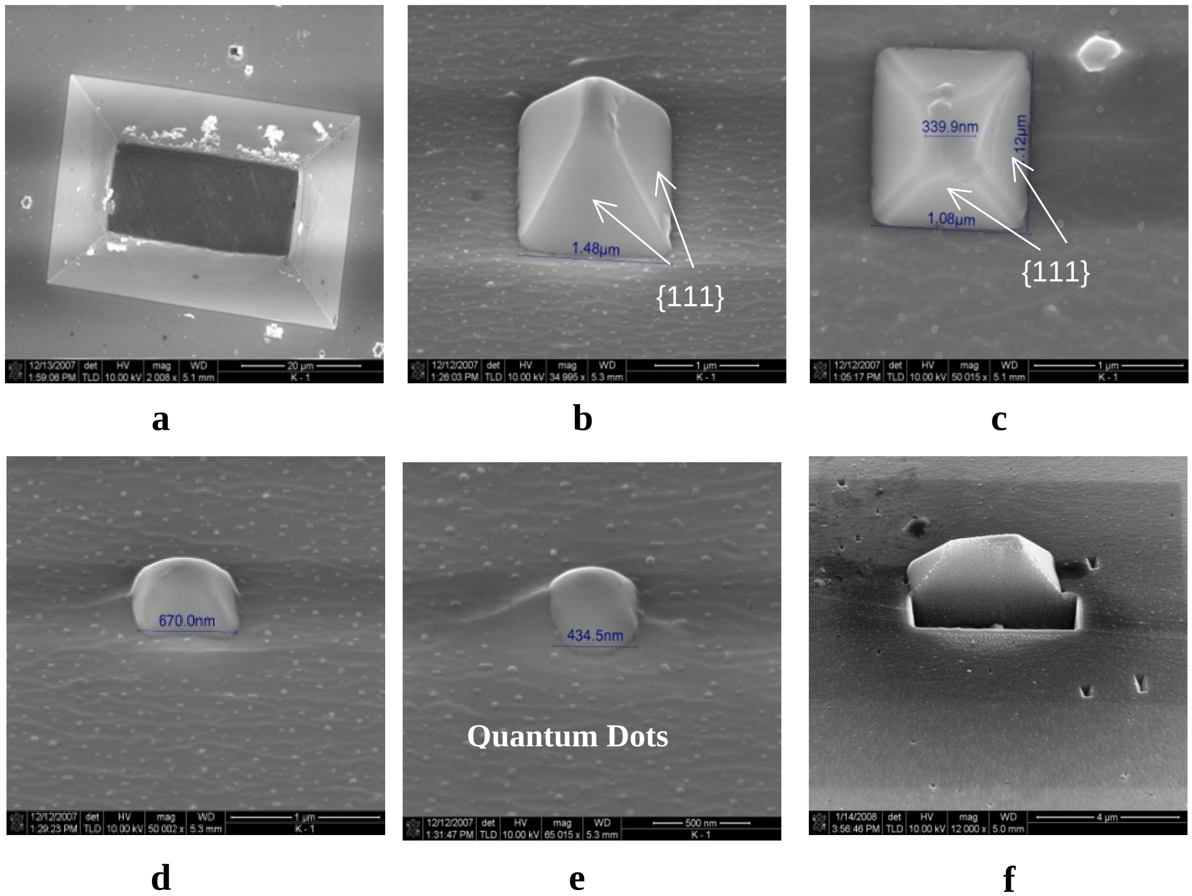



**Fig. 3.** The self-assembled InAsSbP-based strain-induced islands grown by liquid phase epitaxy on InAs substrate and their evolution from the pyramid to globe – a, b, c, d, e; f – pyramid cut by Focused Ion Beam.

For investigation of these islands the Scanning Electron Microscope (SEM-EDAX – FEI Nova 600–Dual Beam) interconnected with the Focused Ion Beam (FIB) technique was employed. Certainly, the TEM measurements are more convenient method for investigation of such type of objects. But for the time being we decided to apply the following approach for the *in situ* investigation of composition, elastic strength (lattice mismatch ratio) and the shape transformation of these pyramids. At first, the three pyramids – “large”, “middle” and “small” with the bottoms length of 6, 5 and 1 μm respectively have been selected. Then these pyramids were cut by FIB technique in high vacuum (See Fig. 3 f). After turning of whole sample the cross-sectional SEM – EDAX measurements from the pyramids top and bottom’s two opposite angles have been *in-situ* carried out. Taking into account the penetration depth and using the electron probe point microanalysis the following X-ray lines were detected: In–L(α), As–L(α), Sb–L(α), P–K. The standard quantitative analyses of spectra at acceleration voltage of 10 kV were done. Acquisition time was 5 s for every spectrum. The compositions of quaternary $InAs_{1-x-y}Sb_xP_y$ pyramids with the values of $x < 4$ at.% and $y < 2$ at.% were measured. The good symmetry of compositions and lattice mismatch ratio values in the both angles of cut pyramid's base has been detected.

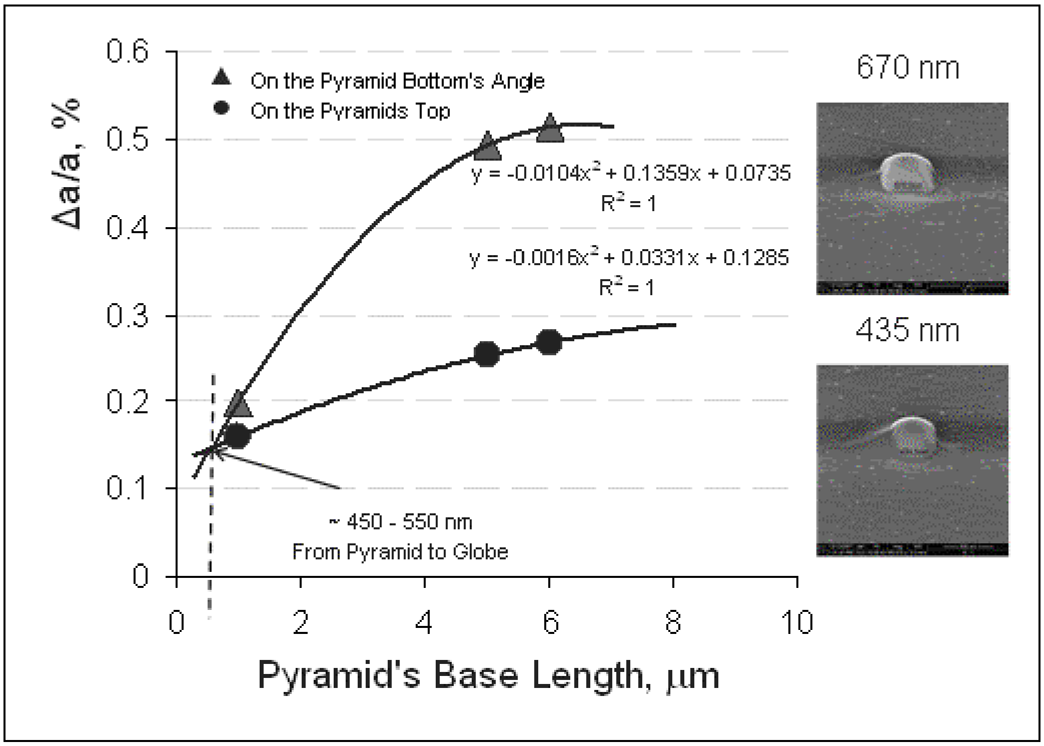



**Fig. 4.** Dependence of lattice mismatch ration on the bottom and top of InAsSbP-based strain induced pyramids versus to their base length.

On the base of SEM-EDAX measurements data and using the Vegard's law the lattice constant at measured point of InAsSbP quaternary pyramids and corresponding lattice mismatch ratio ( $\Delta a / a$ ) with the InAs substrate were calculated. Investigations shown, that the strength on the top of pyramids was less than on the bottom's angles and that the size of islands becomes smaller when the lattice mismatch decreases. In Fig. 4 the dependence of lattice mismatch ratio on the pyramid bottom's angle and separately on the top for three "large", "middle" and "small" InAsSbP strain induced pyramids versus to their base length is presented. The polynomial approximations of experimental data were done and the cross point ($L_{Critical}$ = 510 nm) of these curves was calculated. From our point of view the physical meaning of this critical size is that the island has to change the form from pyramid to globe, because only in this case the strength on the pyramid's bottom can be equal to the strength on top. In the insert of Fig. 4 are presented the SEM pictures of "smallest" pyramid (base length - 670 nm) and globe-shape island (diameter - 435 nm), which confirm our assumption. In order to be sure the whole surface of substrate was checked and the pyramids with the size less than ~ 500 nm have not been detected.

## Conclusion

In this paper we described our first results on application of the Liquid Phase Epitaxy technique for the formation on InAs (100) substrates self-assembled InAsSbP based strain induced islands. The evaluation of these objects from pyramids to globe and quantum dots (QD) was detected and investigated. The morphology, dimensions (size and shape), distribution density and composition of islands were investigated. The EDAX measurements on the top and bottom's angles of InAsSbP quaternary pyramids as well as the lattice mismatch ratio calculations have been carried out. The compositions of quaternary $InAs_{1-x-y}Sb_xP_y$ pyramids with the values of x < 4 at.% and y < 2 at.% were measured. The good symmetry of compositions and lattice mismatch ratio values in the both angles of cut pyramid's base has been detected. Investigations shown, that the strength on the top of pyramids was less than on the bottom's angles and that the size of islands becomes smaller when the lattice mismatch decreases. The average density of the QDs was equal (5-7) $\times 10^9$ $cm^{-2}$, with dimensions of 0, 7-12 nm in height and 20-80 nm in width. The Gaussian distribution of QD's amount versus to their average diameter has been also detected. The critical size ($L_{Critical}$ ~ 500 nm) of InAsSbP-based strain induced pyramid's shape transformation to globe was determined. Our further investigations will be focused on the measurements and investigations of low temperature optical characteristics (photoluminescence, electroluminescence, transmission spectra, etc.) of QDs and fabrication of p-InAsSbP/n-InAs lattice matched diode heterostructures with the QDs inside p-n junction spatial charge region for several mid-infrared applications.

## Acknowledgments

The authors wish to thank Prof., Dr. R. Fornari for help, support and fruitful discussion. This work was carried out in the frame of Armenian National Governmental Program for Nano-Electronics and Nano-Technology and ISTC Grant A – 1232.

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