Overview of InAs-based III-V Compound and Si/Ge Semiconductor Epitaxial Strain-Induced Islands and Quantum Dots Grown by Liquid Phase Epitaxy

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Abstract

The brief overview of InAs-based III-V compound and Si/Ge semiconductor epitaxial strain-induced islands and quantum dots (QD) grown by Liquid Phase Epitaxy (LPE) and other techniques is presented. The main technological modes for fabrication of strain-induced islands and QDs are described. Our latest investigations and results for the growth of the self-assembled InAsSbP-based strain-induced islands and QDs on InAs(100) substrates by LPE technique are summarized. Here we show that such islands, as they decrease in size, are undergoing a shape transition. As the islands volume decreases, the following succession of shape transitions are detected: truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", which gradually evolve to semiglob and then to QD. The morphology, size, shape and composition of these objects are investigated by scanning electron microscope (SEM-EDAX-FEI Nova 600-Dual Beam), interconnected with the Focused Ion Beam (FIB) technique, energy dispersive X-Ray analysis (EDXA) technique and atomic force microscopy (AFM-TM Microscopes-Autoprobe CP). A critical size (~550 nm) of the InAsSbP-based strain-induced islands shape transformation from "prepyramid" to semiglobe is experimentally detected and, in addition, theoretically explained and calculated. Proposed theoretical approach has been also employed and tested for $Si_{1,x}Ge_x$ model system islands grown on a Si(001) substrate. It is shown that for both materials theoretically calculated values of the critical size coincide with experimentally obtained data. EDAX measurements at the top and bottom's angles of the InAsSbP quaternary pyramids and lattice mismatch ratio calculations have been performed. These measurements showed that the strength at the top of pyramids is lower than at the bottom's angles, and that the islands size becomes smaller when the lattice mismatch decreases. The LPE technological conditions for the fabrication of quaternary InAsSbP QDs on InAs(100) substrate are described. The QDs average density ranges from 5 to 7×10^9 cm⁻², with heights and widths dimensions from 0.7 nm to 25 nm and 20 nm to 80 nm, respectively. The Gaussian distribution of QD's amount versus to their average diameter has been experimentally detected. The transmission spectra at room temperature of an unencapsulated InAsSbP QDs by the Fourier-Transform Infrared Spectrometry (FTIR-Nicolet/NEXUS) were investigated. The displacement of absorption edge toward the long wavelength region from $\lambda = 3.44 \ \mu m$ (for InAs test sample) to $\lambda = 3.85 \ \mu m$ (for InAs with QDs) has been detected.

Key Words: Liquid Phase Epitaxy, Self-Assembled, Strain-Induced, III–V Compounds Semiconductors, Pyramids, Quantum Dots

1. INTRODUCTION

In recent years, a large research effort has been devoted to quantum dots (QDs) and quantum wires [1–6] due to their modified density of states, fascinating optoelectronic properties and device applications in areas such as lasers, photodetectors and other electronic devices. From electronic device applications point of view, it is valuable to fabricate QD devices based on processing techniques compatible with very large-scale integrated circuits. Among quantum dots and wires fabrication techniques, the self-organized Stranski-Krastanow method [7] 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 to 30 nm wide and 0.6 to 8 nm high, depending on the material and growth conditions) and homogeneous (the size distribution has a broadening of about 15%) that they exhibit a strong 3D confinement and behave as QDs.

The main approaches for the formation of quantum wires and QDs are presented in Fig. 1, i.e. (*i*) by lithography, etching and then lateral overgrowth, (*ii*) by selective growth and growth on patterned surfaces, and (*iii*) by strain-induced self-assembling.



Fig. 1. Different approaches for the formation of quantum wires and QDs.

When depositing heteroepitaxial layers, there is a relatively limited amount of materials combinations that can be grown with closely lattice matched parameters. By combining lattice-mismatched layers, the range of available materials combinations may be increased, at the cost of

incorporating strain into the grown materials. Depending on the amount of strain, the growth can lead to different surface morphologies. Three main growth modes can be identified (Fig. 2).



Fig. 2. Schematics of the three fundamental growth modes at heteroepitaxy.

(*i*) Frank Van-der-Merwe growth mode is the situation when a layer grows in a pure 2D layerby-layer manner. When the sum of the surface free energy (γ_s), for the epitaxial layer and the interface free energy ($\gamma_{s/f}$) is lower than the free energy of the substrate surface (γ_f), it is energetically favorable for the epitaxial layer to completely cover the surface:

$$\gamma_s + \gamma_{s/f} < \gamma_f \,. \tag{1}$$

This mode is performed, for instance, at the growth of AlGaAs layers on GaAs substrate etc.

If the epitaxial layer is lattice mismatched as compared to the substrate, the 2D growth can still continue, since a certain amount of strain can always be accommodated in the epitaxial layer. The epilayer then is deformed elastically, and the in-plane lattice constant of the epilayer is forced to take the same values as the lattice constant for the substrate. Layers under compressive strain $((a_{sub} - a_{epi})/a_{epi} < 0)$ expand in the growth direction, while layers under tensile strain $((a_{sub} - a_{epi})/a_{epi} > 0)$ shrink in the growth direction. The accumulated strain energy increases linearly with the thickness of the deposited layer, and at a certain critical thickness of the epilayer, it cannot accommodate more strain elastically: the epilayer has to find other ways of relieving the strain. One such way of relaxation is the formation of interfacial misfit dislocations, resulting in plastic deformation, which lets the epitaxial layer relax toward its free lattice parameter. This is common for thick layers with a small misfit, or for graded composition layers.

(*ii*) In the case when the surface free energy of the epitaxial layer plus the interface free energy is larger than the substrate surface free energy, it is energetically more favorable to have the substrate surface exposed to the vapor, as compared to the epitaxial layer. This leads to the formation of 3D clusters on the surface, called Volmer–Weber growth mode, usually observed for strained layers with a lattice mismatch more than 10%:

$$\gamma_s + \gamma_{s/f} > \gamma_f. \tag{2}$$

This growth mode is performed, for example, at the epitaxy of GaN on sapphire etc.

(*iii*) For no so high misfit, one way of relaxation is the next fundamental growth mode, represented by the Stranski and Krastanow at 1936 [7], where the sum of the surface free energy and the interface free energy is about the same as the substrate free energy:

$$\gamma_s + \gamma_{s/f} \approx \gamma_f \,. \tag{3}$$

The lattice mismatch in this case is commonly a few percent compressively strained. For example, at the epitaxy of InAs on GaAs, Ge or SiGe alloy on Si substrate, *etc.* A layer, which in a 2D fashion, undergoes a phase transition towards 3D growth as the accommodation of elastic strain in a pseudomorphic layer changes the balance between the surface and interface free energies during growth. This results in the formation of coherent (dislocation-free) islands (QDs) on the top of a thin wetting layer. Depending on the value of strain, the thickness of wetting layer is varied from a few monoatomic layers until few tenths of nanometers. Note, as a curiosity, that in the original publication by Stranski and Krastanow [7], no strain effects were considered.

During epitaxy, the deposition of the island material starts with a complete wetting of the substrate. As the deposition continues, the accumulated strain energy (E_{el}) increases linearly with the wetting layer thickness, according to $E_{el} = c\varepsilon^2 t$, where *c* is the elastic modulus, ε is the lattice mismatch, and *t* is the wetting layer thickness. The deposition rate (R) is constant and therefore E_{el} , and consequently the total energy of the system, increases linearly in time (see Fig. 3).

When the wetting layer thickness exceeds the equilibrium thickness (t_c^e) , the system enters a metastable region. There is potential for island formation, but the activation energy for the formation needs to be overcome. When the critical wetting layer thickness (t_c) is reached, the island nucleation starts and the wetting layer starts to decompose. Mobile adatoms from the decomposing wetting layer stick together with the deposited adatoms at the surface, and island nuclei are formed. When these nuclei become larger than a certain critical size, determined by surface and interface energies and bond strength, they grow steadily. Before the nuclei reach this critical size, they run the risk to dissolve. The shapes of these strain-induced islands and QDs include the arc of a circle, a cone, full or truncated pyramids, and rectangles.



Fig. 3. Schematic of the total energy versus time for the self-assembling process. E_E is the excess energy due to strain and E_A the 2D-3D activation barrier.

In Fig. 4(a) the largest pyramids in Gizah (Egypt) with the height of ~150 meters, and the smallest Ge pyramids (Fig. 4b–4d) with the height of a few nanometers, grown on Si(001) substrate, are presented.



Fig. 4. The largest pyramids in Gizah (Egypt) with the height of ~150 meters (*a*), and the smallest nano-scale Ge pyramids grown on Si(001) substrates (*b-d*).

For fundamental physics, some phenomena such as the interaction between coupled QDs [8] and the resolution of the quantum states in current–voltage characteristics [9] have been also observed. For optoelectronic devices, it is critical to prepare ordered and uniform QDs. So far, various attempts have been undertaken to improve size and site uniformity for self-organized quantum dots [10–12]. 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 better device

performance, such as higher gain, lower threshold currents, less temperature sensitive threshold current and emission wavelength and longer wavelengths to mid-infrared region in lasers. This leads to the increase in the infrared photodetectors response and operating temperature, as well as PV solar cells efficiency [13]. However, the wavelengths of emission and absorption range remain somewhat limited as there are only few systems allowing self-assembled quantum dot formation.

Narrow band-gap III-V semiconductor materials as InAs, GaSb, InSb and their alloys are particularly interesting and useful since they are potentially promising to access mid- and far infrared wavelength regions 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) [14]. In addition, such narrow band gap semiconductors could also exhibit such interesting properties as metal-induced Fermi level pinning very high into the conduction band, leading to 2D electron gas formation [15]. 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, with InP, GaAs, GaSb and InAs used as substrates. InSb [16, 17], InAsSbP [18, 19], InAsSb [20–23], InAlAs [24], InGaAs [25], InAsP [26] and InAs [20, 28, 29] QDs for mid-IR emission and Si-Ge [29] 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 [20]. 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 the 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 only and is therefore well-suited for optoelectronic devices fabrication. However, it is generally 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 [30] and with appropriate LPE modifications has been successfully employed to grow quantum-well heterostructure lasers [31, 32]. Also notice that it is possible to grow chemically abrupt interfaces by LPE and that quantum wells as thin as 20 Å have been successfully prepared [33]. In [34] the first InAs quantum wells with thickness as low as 25 Å grown by LPE using a special rapid slider technique have been reported.

As we already noted, the key parameters of islands are the shape, size distribution, strain and composition which can modify the electronic and optical properties of the final product using in a semiconductor device. Precise control of the growth process is required in order to produce highly regular mono-disperse island arrays. However, many aspects of especially III-V ternary and quaternary compound islands (and then quantum dots) formation and evaluation and other scientific and technological problems are still poorly understood. There is a well-developed understanding of island nucleation [35, 36] and subsequent coarsening [37] for the simple case where islands grow with a fixed shape. But in several cases, bimodal island size distributions have been observed, inconsistent with classic coarsening [38-41]. Recently it has been shown that the bimodal size distribution is directly related to a change in shape of the growing islands [40]. The precise nature of this shape transition has been the subject of some discussion [40, 41]. But it is clear that the shape change is closely related to the problem of obtaining uniform island size distribution [41], a key issue for potential applications of these islands in nano-scale devices. Ge and Si-Ge on Si(001) have been widely used as model systems for understanding islands formation and heteroepitaxy [29, 42, 43]. In particular, a misfit strain drives the formation of epitaxial islands, and there is a great interest in exploiting such "self-assembled quantum dots" in nanoscale technology. This system exhibits many remarkable features. As a model system, it suggests that heteroepitaxy is surprisingly complex. Ge islands were first observed by Mo et al. [42] as {105}-faceted rectangular pyramids. A rich body of subsequent work showed that, in equilibrium, small islands are square pyramids, while larger islands develop a more complex multifaceted shape [40] after passing through a first-order shape transition [35, 41, 43]. The similar shape transition for InGaAs alloy quantum dots grown on a GaAs substrate has been also detected [44]. Several technological growth methods have been applied for the fabrication of such type of islands, in particular, molecular beam epitaxy (MBE) [44], chemical vapor deposition [45], migration enhanced epitaxy (MEE) [44], ultrahigh vacuum magnetron sputtering epitaxy (UHV–MSE) [46] and liquid-phase epitaxy [19, 28].

2. LIQUID PHASE EPITAXY OF InAsSbP STRAIN-INDUCED ISLANDS AND QUANTUM DOTS ON InAs (100) SUBSTRATES

A. Technological Procedures and Experimental Results

InAs and related III-V compound narrow band-gap semiconductors are promising materials for the fabrication of very important for the mid-infrared region applications in optoelectronic semiconductor devices. In this paper, we summarize and report our first example of InAsSbP quaternary self-assembled strain-induced islands and quantum dots growth on InAs(100) substrates by liquid phase epitaxy (LPE).

According to the thermodynamics principles (minimum energy), during the growth on (100) or (001) faceted substrates, as the strain-induced islands volume decreases, the following succession of shape transitions has to be detected: truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", ellipsoidal and then semiglob like object (Fig. 5).



Fig. 5. Shape transition of the strain-induced islands at the decreasing of their volume.

In our experiments the samples are grown by 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 surfaces exhibit a similar shape for an extended concentration range mainly consisting of truncated pyramids with {111} side facets and a {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 is performed in pure hydrogen atmosphere. The InAs(100) substrates have a 11 mm diameter, are undoped, with a background electron concentration of n = 2×10^{16} cm⁻³. The quaternary alloy InAs_{0,742}Sb_{0,08}P_{0,178} used here is conveniently lattice-matched to InAs. We have previously used this alloy for the fabrication of thermophotovoltaic (TPV) cells and mid-infrared diode heterostructures [14].

Our SEM and AFM studies show the formation of InAsSbP quaternary islands and the evolution of their shape from truncated pyramids to semiglobes, which then gradually evolve to ellipsoidal- and globe-shape quantum dot objects (Fig. 6).

Armenian Journal of Physics, vol. 1, issue 4, 2008



Fig. 6. SEM (a – i) and AFM (j – l) images of the self-assembled InAsSbP-based strain-induced islands and QDs grown by LPE on InAs (100) substrate, and their evolution from a truncated pyramid to a quantum dots (j – S=1×1 μ m², 1– S=500×500 nm²).

To expect strain-induced islands and quantum dots formation, we use arsenic undersaturated and antimony supersaturated liquid phase. To provide a lattice mismatch up to 2% between the InAs substrate and InAsSbP epilayer, we use mole fractions of $X_{InAs} = 0,0195$, $X_{Sb} = 0,1228$ and $X_{InP} = 1,7 \times 10^{-4}$ in the growth melt. The LPE growth solution components – undoped InAs, undoped InP and Sb (6N) are solved in a In (7N)-solution which has been first homogenized for one hour at T=580°C and then three hours at the LPE initial growth temperature of T=550°C to equilibrate the system thermodynamically. After, the quaternary liquid phase is brought in contact with the InAs substrate. To initiate the growth of islands and quantum dots, we use an over-saturation by decreasing the initial growth temperature up to 2°C using the slower ramp rate.

We first explore the resulting morphology looking at the quantum dots size, shape and density using AFM (TM Microscopes–Autoprobe CP). The images are acquired at a constant scanning

force using a silicon nitride soft cantilever probe with a pyramidal tip. In order to avoid instrumental artefacts, each investigated area is scanned several times along different directions. Figures 6(j-l) display AFM images of InAsSbP unencapsulated QDs grown by LPE on InAs(100) for surface areas of $S=1\times1 \mu m^2$ (j) and $S=500\times500 \text{ nm}^2$ (l).

The InAsSbP quantum dots are clearly visible and quite uniformly distributed over the substrate surface (Figs. 6j-l). The average QDs density is about $(5-7) \times 10^9$ cm⁻² with heights from 0.7 nm to 25 nm and width ranging from 20 nm to 80 nm. Since the difference in lattice parameter is large enough, the growth process is consistent with the Stranski–Krastanow [7] mechanism. However, we are unable to confirm the presence of a wetting layer without a transmission electron microscopy (TEM) study. The Gaussian distribution of the QDs amount versus their average diameter calculated from the substrate surface S = 4 μ m² was detected and displayed in Fig. 7 showing the optimum size of QDs to be at ~ 50 nm.



Fig. 7. Dependence of the InAsSbP QDs amount versus their average diameter.

Next, we used Fourier-Transform Infrared Spectrometry (FTIR–Nicolet/NEXUS) to investigate at room temperature the transmission spectra of unencapsulated InAsSbP QDs. As a test sample, we used the same undoped InAs substrate without QDs and islands. The results show (Fig. 8) the displacement of absorption edge towards the long-wavelength region from $\lambda = 3.44 \mu m$ (for InAs test sample) to $\lambda = 3.85 \mu m$ (for InAs with QDs).

We performed scanning electron microscopy and Energy Dispersive X-rays Analysis (SEM-EDXA–FEI Nova 600–Dual Beam) interconnected with the Focused Ion Beam (FIB) technique to study the strain-induced InAsSbP-based islands, in particular, their composition, elastic strength (lattice mismatch ratio) and shape transformation. Interestingly enough, these islands primarily grow into pyramids. Their shape is likely due to insufficient growth melt homogenization. In addition, the shapes of these objects include not only pyramids, but also truncated pyramids, ellipsoidal and globe-shape objects.



Fig. 8. FTIR spectra of the InAs test sample and InAs with unencapsulated InAsSbP QDs at room temperature.

First, we select three pyramids – "large", "middle" and "small" having bottoms length of 6, 5 and 1 μ m respectively. Then these pyramids were cut-off by Focused Ion Beam (FIB) technique in high vacuum (see Fig. 9). After turning of whole sample, we perform cross-sectional SEM–EDXA measurements from the pyramids top and bottom's two opposite angles.



Fig. 9. InAsSbP strain-induced pyramids cut-of by FIB technique; (a) pyramid's base length $-1 \mu m$, (b) 5 μm .

Taking into account the penetration depth and using the electron probe point microanalysis, the following X-ray lines are detected: In–L(α), As–L(α), Sb–L(α), P–K, that we use to perform a quantitative spectra analysis at electron energy of 10 keV. Acquisition time is 5 s per spectrum. The quaternary InAs_{1-x-y}Sb_xP_y pyramids compositions are found at values of x < 4 at % and y < 2 at %. The compositions and lattice mismatch ratio exhibit good symmetry values in both angles of cut-off pyramid's base. Based on SEM–EDXA measurements data and using the Vegard's law, we determine the lattice constant at InAsSbP quaternary pyramids and the corresponding lattice mismatch ratio ($\Delta a/a$) with the InAs substrate. Of special interest, the results show that the strength at the top of pyramids is smaller than at its bottom's angles, and that the islands size becomes smaller when the lattice mismatch decreases. Figure 10 displays the dependence of lattice mismatch ratio at the pyramid bottom's angle and separately, at the top of the three "large", "middle" and "small" InAsSbP strain induced pyramids *vs* their base length.



Fig. 10. Dependence of the lattice mismatch ratio on the bottom and top of InAsSbP-based strain induced pyramids *vs* their base length.

The experimental data polynomial approximations (see inserts in Fig. 10) and the crossing point (L _{Critical} = 510 nm) of these curves are now calculated. Since the island is changing from a pyramid to a globe, this physically means that such a critical size can be understood in terms of having the strength at the pyramid's bottom and top to be equal. The SEM measured values of the "smallest" pyramid base length (670 nm – Fig. 6h) and of the globe-shape island diameter (435 nm – Fig. 6i) further support such a scenario. Indeed, when checking the whole substrate surface, we did not found any pyramid having a size smaller than ~ 500 nm.



Fig. 11. Distribution of the local strain energy density before and during island formation – (a), and towards the pyramid's height (3D) – (b).

In Fig. 11 we correspondingly present the distribution of the local strains energy density before and during island formation – (a), and isolated Ge{105} pyramidal hut island grown on Si(100) substrate, colored according to one-half the trace of the calculated in-plane surface strain fields – (b) [29]. It is seen that the maximum of strength takes place at the corners of the pyramid's base and at the pyramid's facets–substrate interface. Then the strain decreases towards the height and accepts the minimum value at the top of pyramid. This result supports a similar scenario obtained in our investigations (see Fig. 10) for quaternary InAsSbP strain-induced island.

Finally, as already mentioned, at LPE process the liquid phase is homogenized for three hours only at initial 550°C growth temperature. A longer time (~8 hours and more) or a multistage liquid phase homogenization should prevent islands formation and/or allow their suppression thereby favoring QDs formation.

B. Shape Transition of InAsSbP Strain-Induced Islands at Liquid Phase Epitaxy on InAs(100) Substrates (Theory)

In order to theoretically explain and quantitatively calculate the critical size of the island shape transformation from pyramid to semiglobe, the following theoretical approach is performed. Here we derive an explicit approximation for the energy, which provides a good explanation of the island shape transition. Generally, the smallest "pre-pyramid" shape consists of four {111} and eight {105} facets at (100) or (001) directed substrate. According to the SEM measurements, for our system the total value of {105} facets surface is negligibly small in comparison with the {111}

facets surface. That is why we assume that our island is a truncated pyramid with the width *s*, length *t* and height *h*, in the *x*-, *y*- and *z*-directions, respectively. We assume also that the pyramid is symmetric and the edge is at an angle θ to the substrate. We take as our energy reference the InAs(100) substrate plus InAsSbP quaternary island strained to match with the substrate in the *x*- and *y*-directions, and free to relax in the *z*-direction.

The island total energy can be written as

$$E = E_{\rm S} + E_{\rm R} + E_{\rm V},\tag{1}$$

where E_S is the extra surface and interface energy, E_R is the energy change due to the elastic relaxation, and E_V is the volume energy. In particular,

$$E_{\rm S} = st(\gamma_i + \gamma_t - \gamma_s) + 2(s+t) \left[h\gamma_e \csc\theta - h\cot\theta(\gamma_t + \gamma_s - \gamma_i)/2\right],\tag{2}$$

where γ_s , γ_t , and γ_e are the surface energy (per unit area) of the substrate and of the island top and edge facets, respectively, and γ_i is the island–substrate interface energy [47].

For the case of coherent Stranski–Krastanow growth, where the strained material wets the surface before forming islands, $\gamma_t = \gamma_s$ and $\gamma_i = 0$, so the surface energy term becomes

$$E_{\rm s} = 2(s+t) h \Gamma, \qquad (3)$$

where $\Gamma = \gamma_e \csc \theta - \gamma_s \cot \theta$.

Generally,

$$\gamma_{\rm s} = \frac{1}{2} C_{\rm ij} \varepsilon_{\rm i} \varepsilon_{\rm j} , \qquad (4)$$

where $C_{i,j}$ (*i*, *j* = 1, ...,6) are the elastic modulus and $\varepsilon = \Delta a/a$ is the relative strain. In order to calculate the energy of elastic relaxation we assume that the composition of multicomponent island does not change in the *z*-direction and that the strain ε is constant, i.e., $\varepsilon_{xz} = \varepsilon_{yz} = 0$. For the crystals with a cubic symmetry

$$\gamma_{\rm s} = \left(\frac{1}{2}C_{11}\frac{\Delta a^2}{a^2} + \frac{1}{2}C_{44}\frac{\Delta a^2}{a^2}\right)d_{\rm wet} , \qquad (5)$$

where d_{wet} is the wetting layer thickness.

Thus, the energy of elastic relaxation is determined by [34]

$$E_{\rm R} = -\frac{1}{2} \int dx \, dx' \, \chi_{\rm ij}(x - x') f_{\rm i}(x) f_{\rm j}(x') \,, \qquad (6)$$

where x and x' are two-dimensional (2D) vectors, $f_i = \partial_j \sigma_{ij}$ is the force density at the surface, and χ is the elastic Green's function of the surface, which describes the linear response to an applied force. Here $\sigma_{ij} = \sigma_b h(x) \delta_{ij}$ is the 2D islands stress tensor, $\sigma_b = C_{ij} \frac{\Delta a}{a}$ is the *xx*- or *yy*-component of the bulk stress of islands uniformly strained to the substrate x and y lattice constants, and allowed to relax in *z*, and h(x) is the height (thickness) of the island at the position *x*.

The analytically evaluated result of integral (6) at the surface Green's function of an isotropic solid [47] can be written as

$$E_R^{\text{pyramid}} = -2ch^2 \left[s \ln(\frac{t}{\phi h}) + t \ln(\frac{s}{\phi h}) \right] , \qquad (7)$$

where $c = \sigma_b^2 (1-\nu)/2\pi\mu$ and $\phi = e^{-3/2} \cot \theta$. Here $\nu = \frac{\lambda}{2(\lambda + \mu)}$ is the Poisson ratio, μ and λ are the Lame coefficients, and $h = \frac{b_1 - b_2}{2} \tan \theta$, $t = s = \frac{b_1 + b_2}{2}$, where b_1 and b_2 are the lengths of truncated pyramid base and top, correspondingly.

Thus, the pyramid total energy can be written as

$$E^{\text{pyramid}} = E_{\text{S}} + E_{\text{R}} = -\frac{c}{2} (b_1 - b_2)^2 (b_1 + b_2) \tan^2 \theta_p \left(\ln \frac{b_1 + b_2}{b_1 - b_2} + \frac{3}{2} \right) + (b_1^2 - b_2^2) \left(\frac{1}{\cos \theta_p} \gamma_e - \gamma_s \right), \quad (8)$$

where $\theta_{\rm P}$ is the angle between the pyramid edge and the substrate surface.

For calculation of the glob-shape island total energy we perform the following approach. Using expression (7) at $b_2 = 0$, $b_1 = s = t = D$ and h = D/2, where D is the diameter of semiglobe, the elastic relaxation and surface energy of the glob-shape island can be written as

$$E_{\rm R}^{\rm globe} = -cD^3 \left(\frac{3}{2} - \ln\frac{\cot\theta_{\rm G}}{2}\right) \tag{9}$$

$$E_{\rm S}^{\rm globe} = \frac{\sigma S_{\rm globe}}{2} = \frac{\sigma \pi D^2}{2} , \qquad (10)$$

where σ is the density of the globe surface energy and θ_G is the angle between the tangent to the semiglobe and the substrate surface.

The island's volume energy is determined as a sum of the chemical potentials of each component, and since at the critical volume, when island changes the shape from pyramid to semiglobe, the number and type of components are the same, then we have

$$E_{\rm V}^{\rm pyramid} = E_{\rm V}^{\rm globe} \,. \tag{11}$$

Finally, the energy equilibrium condition can be written as

$$E_{\rm S}^{\rm pyramid} + E_{\rm R}^{\rm pyramid} = E_{\rm S}^{\rm globe} + E_{\rm R}^{\rm globe} , \qquad (12)$$

or in bare view

$$-\frac{c}{2}(b_{1}-b_{2})^{2}(b_{1}+b_{2})\tan^{2}\theta_{p}\left(\ln\frac{b_{1}+b_{2}}{b_{1}-b_{2}}+\frac{3}{2}\right)+\left(b_{1}^{2}-b_{2}^{2}\right)\left(\frac{1}{\cos\theta_{p}}\gamma_{e}-\gamma_{s}\right)=$$

$$=-cD_{cr}^{3}\left(\frac{3}{2}-\ln\frac{\cot\theta_{G}}{2}\right)+\frac{\sigma\pi D_{cr}^{2}}{2},$$
(13)

where D_{cr} is the critical diameter when the island shape is changed from pre-pyramid to semiglobe.

For the calculation of numerical values of some parameters, in particular, the elastic modulus and the density of surface energy and other parameters for the InAsSbP quaternary alloys, we employed the following linear approximation:

$$P(\text{InAs}_{1-X-Y}\text{Sb}_X\text{P}_Y) = P^{\text{InAs}}(1-X-Y) + XP^{\text{InSb}} + YP^{\text{InP}}.$$
(14)

The appropriate calculated values for $InAs_{1-x-y}Sb_xP_y$ islands grown on InAs(100) substrate and $Si_{1-x}Ge_x$ islands grown on Si(001) substrates, as well as the literature data for InAs, InSb, InP, Si and Ge are presented in Table 1.

It is well known that the transmission electron microscopy (TEM) is the most useful technique for determination of the wetting layer thickness. The measured values for some III–V compound semiconductors are presented in Fig. 12. In order to determine the wetting layer thickness (d_{wet}) for quaternary InAsSbP used in this work, as well as for SiGe-based islands, the following approach has been performed. At first, by exponential function we perform the mathematical approximation of experimental data and create the analytic expression (15), which describes the dependence of wetting layer thickness (in monolayers) versus the relative lattice mismatch ratio (in percent):

$$d_{\rm wet} = 25.232 \ e^{-0.3584 \frac{\Delta a}{a}}.$$
 (15)

The approximation accuracy is equal to $R^2 = 0.9988$. The corresponding calculated values for d_{wet} are also presented in Table 1.

TABLE 1.

	InAs	InSb	InP	InAs _{1-x-y} Sb _x P _y x=0.04; y=0.02	Si	Ge	Si _{1-x} Ge _x x=0.3	Si _{1-x} Ge _x x=0.5
$C_{11} \times 10^{-12}$, dyn/cm ²	8.329	6.669	10.11	8.267	1.657	1.26	1.538	1.458
$C_{12} \times 10^{-12}$, dyn/cm ²	4.526	3.645	6.61	4.538	0.639	0.44	0.5793	0.5395
$C_{44} \times 10^{-12}$, dyn/cm ²	3.959	3.626	4.56	3.9564	0.796	0.677	0.7603	0.7365
d _{wet} , nm		1.266	4.866	14.29		3.234	8.581	6.767
$\sigma \times 10^7$, J/cm ²	752			~ 752	310	181	219	245



Fig. 12. Dependence of the wetting layer thickness on strain; circles – experimental data, dashed line – mathematical approximation.

Thus, solving the equation (13) at $b_1 = 670 \text{ nm}$, $b_2 = 150 \text{ nm}$, $\gamma_e = 5 \times 10^{-5} \text{ J/cm}^2 [48]$, $\lambda = \frac{1}{5} (2C_{11} + 3C_{12} + 4C_{44}) = 9.195 \times 10^{12} \text{ dyn/cm}^2$, $\mu = \frac{1}{10} (8C_{44} + C_{11} - C_{12}) = 3.537 \times 10^{12} \text{ dyn/cm}^2$,

$$\gamma_{\rm s} = \left(\frac{1}{2}C_{11}\frac{\Delta a^2}{a^2} + \frac{1}{2}C_{44}\frac{\Delta a^2}{a^2}\right)d_{\rm wet} = 3.42 \times 10^{-6}\,\rm{J/cm^2}\,, \qquad \nu = 0.361\,, \qquad \sigma_{\rm b} = 1.65 \times 10^{10}\,\rm{dyn/cm^2}\,,$$

 $c=0.784 \text{ J/cm}^3$, $\theta_{\rm G}=25^{\circ}$, $\theta_{\rm P}=40^{\circ}$, $\frac{\Delta a}{a}=2\times10^{-3}$, the critical size (diameter) of $d_{\rm cr}\approx550 \text{ nm}$ for InAsSbP islands shape transformation from truncated "pre-pyramid" to semiglobe is determined. This value exactly coincides with the experimental result (Fig. 6h–6i).

We have performed the same calculations also for $Si_{1-x}Ge_x$ model system islands grown on Si(001) substrate at x = 0.3 and x = 0.5.

At x=0.3, $b_1 = 95 \text{ nm}$, $b_2 = 5 \text{ nm}$, $\gamma_e = 8 \times 10^{-5} \text{ J/cm}^2 [48]$, $\lambda = 1.57 \times 10^{12} \text{ dyn/cm}^2$, $\mu = 7.046 \times 10^{11} \text{ dyn/cm}^2$, $\gamma_s = 14.4 \times 10^{-6} \text{ J/cm}^2$, v = 0.345, $\sigma_b = 1.92 \times 10^{10} \text{ dyn/cm}^2$, $c = 5.495 \text{ J/cm}^3$, $\theta_G = 4^o$, $\theta_P = 70^o$, $\frac{\Delta a}{a} = 1.25 \times 10^{-2}$, coupled with the parameters presented in Table 1, the critical diameter is equal to $d_{cr} \approx 70 \text{ nm}$. And for x=0.5, $b_1 = 45 \text{ nm}$, $b_2 = 15 \text{ nm}$, $\gamma_e = 8 \times 10^{-5} \text{ J/cm}^2 [48]$, $\lambda = 1.49 \times 10^{12} \text{ dyn/cm}^2$, $\mu = 6.8 \times 10^{11} \text{ dyn/cm}^2$, $\gamma_s = 2.96 \times 10^{-6} \text{ J/cm}^2$, v = 0.343, $\sigma_b = 3.04 \times 10^{10} \text{ dyn/cm}^2$, $c = 14.22 \text{ J/cm}^3$, $\theta_G = 9^o$, $\theta_P = 65^o$, $\frac{\Delta a}{a} = 2 \times 10^{-2}$, $d_{cr} \approx 40 \text{ nm}$. These both calculated values also coincide with experimentally obtained results [14].

3. CONCLUSIONS

Thus, the brief overview of InAs-based III-V compound and Si/Ge semiconductor epitaxial strain-induced islands and quantum dots (QD) grown by Liquid Phase Epitaxy (LPE) and other techniques is presented. The main technological modes for fabrication of strain-induced islands and QDs are described. In this paper our latest investigations and results for the growth of the self-assembled InAsSbP-based strain-induced islands and QDs on InAs(100) substrates by LPE technique are summarized. Here we show that such islands, as they decrease in size, are undergoing a shape transition. As the islands volume decreases, the following succession of shape transitions has been detected: truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", which gradually evolves to semiglobe and then to QD. The morphology, size, shape and composition of these objects are investigated by scanning electron microscope (SEM-EDAX–FEI Nova 600–Dual Beam), interconnected with the Focused Ion Beam (FIB) technique, energy dispersive X-Ray analysis (EDXA) technique and atomic force microscopy (AFM–TM Microscopes–Autoprobe CP). A critical size (~550 nm) of the InAsSbP-

based strain-induced islands shape transformation from "pre-pyramid" to semiglobe is experimentally detected and, in addition, theoretically explained and calculated. Proposed theoretical approach has been also employed and tested for Si_{1-x}Ge_x model system islands grown on a Si(001) substrate. It is shown that for both materials theoretically calculated values of the critical size coincide with experimentally obtained data. EDAX measurements at the top and bottom's angles of the InAsSbP quaternary pyramids and lattice mismatch ratio calculations have been performed. These measurements showed that the strength at the top of pyramids is lower than at the bottom's angles, and that the islands size becomes smaller when the lattice mismatch decreases. The LPE technological conditions for the fabrication of quaternary InAsSbP QDs on InAs(100) substrate are described. The QDs average density ranges from 5 to 7×10^9 cm⁻², with heights and widths dimensions from 0.7 nm to 25 nm and 20 nm to 80 nm, respectively. The Gaussian distribution of QD's amount versus to their average diameter has been experimentally detected. The transmission spectra at room temperature of an unencapsulated InAsSbP QDs by the Fourier-Transform Infrared Spectrometry (FTIR-Nicolet/NEXUS) were investigated. The displacement of absorption edge towards the long wavelength region from $\lambda = 3.44 \ \mu m$ (for InAs test sample) to $\lambda =$ 3.85 µm (for InAs with QDs) has been detected.

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