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Strain-induced islands and nanostructures shape transition's chronology on InAs (100) surface

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Abstract. The self-assembled strain-induced sub-micrometric islands and nanostructures are grown from In-As-Sb-P quaternary liquid phase on InAs (100) substrates in Stranski-Krastanow growth mode. Two samples are under consideration. The first sample consists of unencapsulated islands and lens-shape quantum dots (QDs) grown from expressly inhomogeneous liquid phase. The second sample is an n-InAs/p-InAsSbP heterostructure with QDs embedded in the *p-n* junction interface. The morphology, size and shape of the structures are investigated by high-resolution scanning electron (SEM) and transmission electron (TEM) microscopy. It is shown that islands, as they decrease in size, undergo shape transitions. Particularly, as the volume decreases, the following succession of shape transitions are detected: sub-micrometric truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", hemisphere, lens-shaped QD, which then evolves again to nano-pyramid. A critical size of 5±2 nm for the shape transformation of InAsSbP-based lens-shaped QD to nano-pyramid is experimentally measured and theoretically evaluated.

Keywords: strain-induced; pyramids; quantum dots; shape transition; III-V semiconductors

1. Introduction

In the last two decades, self-organized nanostructures, especially quantum dots (QDs) grown epitaxially on a semiconductor substrate have been the subject of intense research. Using several technologies, crystal growers have managed to tailor the size, the shape, and the material composition of such structures according to demands coming from their future application in optoelectronic devices, electronic storage and other semiconductor devices, for quantum computation and spintronics (Bimberg *et al.* 1998). In Stranski–Krastanow growth mode (Stranski and Krastanow 1938) the size, geometric structure and composition of self-organized QDs are

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affected both during the first stage of the growth procedure – the deposition of a strained wetting layer which induces the formation of three-dimensional islands, as well as by the second stage – the overgrowth of those islands by a capping layer. Moreover, there are many experimental evidences pointing to the fact that even at simple "pure" material systems, for instance Ge on a Si substrate, or InAs on a GaAs surface, intermixing between the QD material and the matrix occurs to a varying degree, depending on the growth method, temperature, deposition rates, etc (Liu *et al.* 2000). Acknowledging the modification that the QDs shape, size distribution, strain and composition can bring to the electronic and optical properties upon application in a semiconductor device, precise control of the growth process is required to produce uniform and highly regular mono-dispersed island arrays. There is a well-developed understanding of island nucleation (Daruka *et al.* 1999, Tersoff and LeGoues 1994) and subsequent coarsening (Zinke-Allmang 1992) for the simple case where islands grow with a fixed shape. However, in several cases, bimodal island size distributions have been observed, inconsistent with classic coarsening (Reaves *et al.* 1993, Ponchet *et al.* 1995, Medeiros-Ribeiro *et al.* 1998, Ross *et al.* 1998). Recently it has been shown that the bimodal size distribution is directly related to a change in shape of growing islands (Medeiros-Ribeiro *et al.* 1998). The precise nature of shape transition and the problem of obtaining uniform island size distribution have been the subject of some discussions (Medeiros-Ribeiro *et al.* 1998, Ross *et al.* 1998). Ge and Si-Ge on Si (001) have been widely used as model systems for understanding islands' formation and heteroepitaxy (Mo *et al.* 1990, Tersoff *et al.* 2002, Hanke *et al.* 2004). However, they suggest that even at those simple material systems, heteroepitaxy is surprisingly complex. Ge islands were first observed by Mo *et al*. (1991) 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 (Medeiros-Ribeiro *et al.* 1998) after passing through a first-order shape transition (Daruka *et al.* 1999, Ross *et al.* 1998, Tersoff *et al.* 2002). The similar shape transition for InGaAs alloy QDs grown on a GaAs substrate has also been detected (Liu *et al.* 2000). Several technological growth methods have been applied for the fabrication of such type of islands, in particular, molecular beam epitaxy (MBE) (Liu *et al*. 20003), chemical vapor deposition (Ross *et al.* 1998), ultrahigh vacuum magnetron sputtering epitaxy (UHV-MSE) (Rastelli *et al.* 2003), liquid-phase epitaxy (Hanke *et al.* 2004, Gambaryan *et al.* 2008) and droplet epitaxy (Wu *et al.* 2010).

In this paper we present the chronology of InAsSbP composition strain-induced islands shape transition from micrometric truncated pyramids to nanopyramids on InAs (100) surface along with quantitative evaluation of the critical size for the last transformation from lens-shaped QD to nanopyramid.

2. Experimental

Islands and nanostructures were grown from In-As-Sb-P quaternary liquid phase on InAs (100) substrates in Stranski-Krastanow growth mode using the modified slide-boat crucible for the liquid phase epitaxy (LPE). There are two samples under consideration in this work. The first sample consists of unencapsulated islands and lens-shaped QDs grown from the expressly inhomogeneous liquid phase. The technological idea was to provide a different lattice constant value of the wetting layer across the substrate surface. Mole fractions of the quaternary liquid phase components were taken as X_{InAs}=0.0195, X_{Sb}=0.1228, and X_{InP}=1.7×10^{-4} to provide a lattice mismatch up to 2% between the wetting layer and the InAs substrate. The nucleation process was performed at

T=550^{o}C constant temperature under the pure hydrogen atmosphere. The second sample is an n-InAs/p-InAsSbP heterostructure with QDs embedded into the p-n junction interface. This sample was grown by two steps at single technological process using two liquid phases. First, QDs were nucleated from the homogenized and uniform liquid phase on the InAs (100) epi-ready substrate surface at isothermal conditions. Then the liquid phase was changed and the p-InAsSbP cap epilayer was grown by step-cooling version of LPE at ΔT=8^{o}C to provide 4 μm of layer thickness. The high-resolution scanning electron (HR-SEM: FEI Nova 600–Dual Beam) and transmission electron (TEM) microscopes were used for characterization.

3. Results and discussion

The high-resolution SEM images of self-assembled InAsSbP composition strain-induced micro- and sub-micrometric islands are presented in Fig. 1 (a)-(h). TEM images of the single lens-shape QD's and the second sample's cross-sectional area are presented in Fig. 1(j) and Fig. 1(k), (l), respectively.

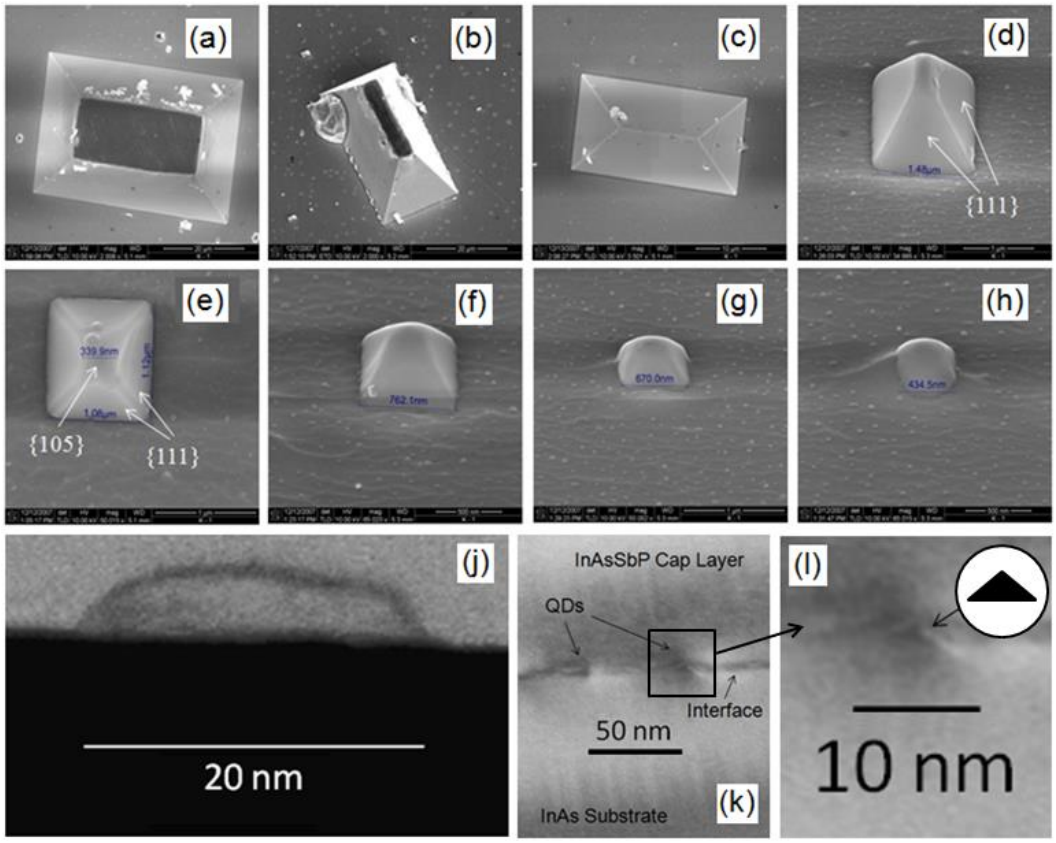

Fig. 1 The self-assembled InAsSbP strain-induced islands shape transition's chronology: from micrometric truncated pyramid to nanopyramid. (a)-(h) - high-resolution SEM images, (j)-(l) - TEM images

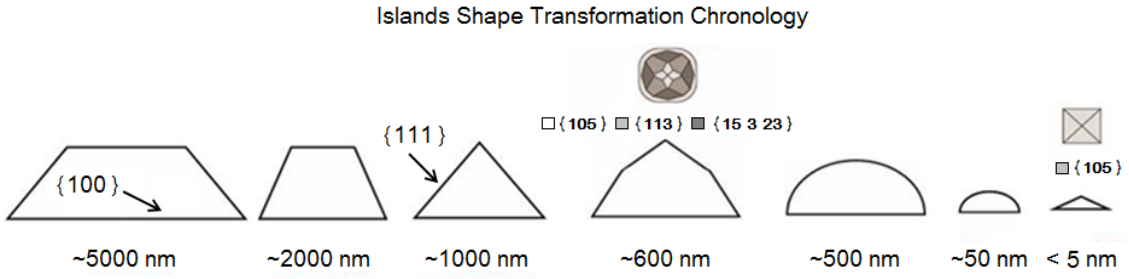

Fig. 2 A schematic representation of islands shape transition chronology

From Fig. 1, it is quite visible that islands, as they decrease in size, are undergoing a shape transition in the following succession: micro- and submicrometric truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", hemisphere, lens-shaped QD, which then evolves into nanopyramid. A schematic of islands shape transition chronology with experimentally measured sizes is presented in Fig. 2.

From Fig. 1 we assert that the first transition from sub-micrometric "smallest" pyramid (670 nm – Fig. 1(g)) to spherically shaped island (435 nm – Fig. 1(h)) occurred at the size of around 500 nm. The critical size of ~550 nm for that shape transformation has been partially measured and theoretically calculated in our previous works (Gambaryan *et al.* 2008a, b). However, TEM measurements of the second sample's cross-sectional area show (Fig.1 (k), (l)) that QDs embedded into the substrate – cap epilayer interface (*p-n* junction spatial charge region) are also pyramidal with the base length of a few nanometers. We assume that at a further decrease in the islands' volume, the second shape transition from lens-shaped QDs to pyramidal QDs occurs.

In addition, the SEM–EDAX measurements show that pyramids have a quaternary composition with higher concentration of antimony (~4–8 atomic %, depending on the pyramid's size) at the pyramid's corners and the minimum value at the center of the truncated pyramid's upper plane.

In order to theoretically explain and quantitatively evaluate the critical size of the last shape transformation, we apply the similar approach described in (Gambaryan *et al.* 2008b, Tersoff *et al.* 1993). However, we adapt to solving an opposite task, i.e., when shape transformation occurs from lens-shape QD to nanometric rectangular pyramid.

We derive an explicit approximation for the energy, which provides good explanation of island shape transition. In our calculation, we assume that the smallest pyramid shape consists of four {105} facets at (100) directed substrate and that the cross section is an equilateral triangle with the base *b*. The island's total energy can be written as

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

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 our case, at the coherent Stranski-Krastanow growth mode, where the strained material wets the surface before forming islands, the surface energy term can be written as (Tersoff *et al.* 1993)

$$E_S^{\,pyramid} = \frac{2\sqrt{3}}{3} b^2 \Gamma, \tag{2}$$

where $\Gamma=\gamma_e \csc\theta - \gamma_S \mathrm{ctg}\theta$, θ is an angle between the pyramid's edge and the substrate, γ_S, and γ_e are

the surface energy (per unit area) of the substrate and island's edge facets, respectively (Tersoff *et al.* 1993).

Generally (Daruka *et al.* 1999)

$$\gamma_{\mathrm{s}} = \frac{1}{2} C_{\mathrm{ij}} \varepsilon_{\mathrm{i}} \varepsilon_{\mathrm{j}}, \tag{3}$$

where $C_{\mathrm{i,j}}$ (i, j=1, ...,6) are the elastic modulus and $\varepsilon=\Delta a/a$ is the relative strain (lattice mismatch ratio between the substrate and the wetting layer). In our approach, we assume that the composition of multicomponent island does not change in z-direction (perpendicular to the substrate surface). In that case, for the crystals with a cubic symmetry

$$\gamma_{\mathrm{s}} = \frac{1}{2}\left(C_{11} + C_{44}\right)\varepsilon^2 d_{\mathrm{wet}}, \tag{4}$$

where d_{wet} is the wetting layer thickness. According to (Daruka *et al.* 1999, Tersoff *et al.* 1993), the elastic strain relaxation energy for the pyramid can be presented as

$$E_R^{pyramid} = -2c\frac{b^3}{3}\ln\frac{\sqrt{3}}{2\phi_P}, \tag{5}$$

where c is the constant determined through the Poisson ratio and the Lame coefficients (Daruka *et al.* 1999, Tersoff *et al.* 1993), $\phi_P=e^{-3/2}\mathrm{ctg}\theta$.

Considering lens-shape QDs as a spherical segment (Fig. 1(j)) with the base diameter of D, corresponding energies can be written as

$$E_S^{lens-shape} = \pi\sigma D^2 \frac{1-\cos\theta_G}{2\sin^2\theta_G} \tag{6}$$

$$E_R^{lens-shape} = -\frac{cD^3}{4}\ln\frac{4}{\phi_L}, \tag{7}$$

where σ is the QD's surface energy density, θ_G is an angle between the substrate surface and the tangent to the segment's surface, and $\phi_L=e^{-3/2}\mathrm{ctg}\theta_G$.

The island's volume energy is the sum of chemical potentials of each component. In addition, the number and type of components remain unchanged when shape transformation occurs. Therefore, we assume that

$$E_{\mathrm{V}}^{\mathrm{pyramid}} = E_{\mathrm{V}}^{\mathrm{lens\text{-}shape}}. \tag{8}$$

Finally, the energy equilibrium condition can be written as

$$\pi\sigma D^2 \frac{1-\cos\theta_G}{2\sin^2\theta_G} - \frac{cD^3}{4}\ln\frac{4}{\phi_L} = \frac{2\sqrt{3}}{3}b^2\left(\gamma_e \csc\theta - \frac{1}{2}\varepsilon^2 d_{wet}\left(C_{11}+C_{44}\right)ctg\,\theta\right) - 2c\frac{b^3}{3}\ln\frac{\sqrt{3}}{2\phi_P}, \tag{9}$$

where b, is the critical size when the transition from lens-shape to nanopyramid occurs. For our InAsSbP material system, from Eq. (9) we evaluate the value of b_{critical}=5±2 nm taking into account accuracy and variation of elastic modulus and the surface energy values. Calculation was performed at D=2×10^{-6} cm, γ_e=5×10^{-5} J/cm^2 (Safonov *et al.* 2007), c=0.784 J/cm^3, θ=60^0, θ_{G}=40^0,

ε=0.025, d_{wet}=10^{-7} cm (Gambaryan *et al*. 2008b), C_{11}=6.67×10^5 J/cm^3, C_{44}=3.63×10^5 J/cm^3 and σ=1.45×10^{-6} J/cm^2 (Safonov *et al.* 2007). Evaluated numerical value for $b_{critical}$ is very close to our experimental result (Fig. 1(j)) and coincides also with the result obtained by Kratzer *et al* (2006).

5. Conclusions

Thus, the self-assembled InAsSbP composition micrometric, sub-micrometric strain-induced islands and nanostructures were grown from In-As-Sb-P quaternary liquid phase on InAs(100). Using high-resolution SEM and TEM microscopes, the chronology of islands' shape transition from micrometric pyramids to nano-pyramids was described. It was shown, that as the island's volume decreases, the following succession of shape transitions is occurred: micrometric, sub-micrometric truncated pyramid, {111} facetted pyramid, {111} and partially {105} facetted pyramid, completely unfacetted "pre-pyramid", hemisphere, lens-shape QD, which then evolves again to nano-pyramid. A critical size of 5±2 nm for the shape transformation of InAsSbP-based lens-shaped QD to nano-pyramid was experimentally measured and theoretically evaluated.

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