NUCLEATION MECHANISM OF STRAIN-INDUCED InAsSbP QUANTUM DOTS AND PITS AT LIQUID PHASE EPITAXY ON InAs (100) SUBSTRATE

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1. Introduction

Recently, a large research effort has been devoted to quantum dots (QDs), quantum wires and pits (QPs) [1-3] due to their modified density of states, fascinating optoelectronic properties and device applications for lasers, photodetectors and other electronic devices. Among quantum dots, pits and wires fabrication techniques, the self-organized Stranski-Krastanow method [4] is an important one by which dislocation-free dots, elongated islands and wires can be produced. The elastic strain caused by lattice mismatch can be also relaxed by the formation of undulations, pits and their combination [5]. On the basis of an atomistic model, it is shown that the energy change due to the step formation is negative or positive depending upon the sign of the misfit. The step formation energy can even be negative for compressive misfit stress in the heterolayer, while it is definitely positive for tensile misfit stress. Depending on the growth conditions, the elastic strain can be relaxed by the formation of either quantum wires and quantum dots, or even unique island-pit pairs. InAsSbP is a promising candidate because it can cover the 3–5 μm mid-infrared regions by adjusting of alloy composition. In spite of some miscibility gap problems, the InAsSbP material system has a fairly large growth window, a very wide range of energy gap and lattice constant values. Two binary substrates can be matched with this quaternary alloy: InAs and GaSb. However, InAs substrates were used because they are less expensive and have higher quality in comparison with GaSb substrates.

In this paper, the nucleation mechanism of strain-induced InAsSbP QDs and QPs at liquid phase epitaxy on InAs(100) substrate is discussed, as well as the immiscibility task for pseudo-ternary InAs – InSb – InP system is presented and analyzed.

2. Quantum dots–pits competing nucleation mechanisms in strain-induced InAsSbP system

Application of the InAsSbP and other similar quaternary materials open up interesting physical and technological prospects for the controlled growth of QDs, QPs and dots–pits cooperative systems. At the growth of lattice matched with the substrate heterolayers from the quaternary liquid phase, corresponding variation of the third and fourth components allows

providing needed sign of the misfit, i.e. to provide tensile or compressive misfit stress. At the first case elastic strain will relax by the formation of QDs, but at the second one – by QPs. At the description of the competing nucleation mechanisms we assume that the surface has only discrete orientations and that only one angle should be considered [6], so InAsSbP-based QDs and QPs have the shape presented in Fig. 1.
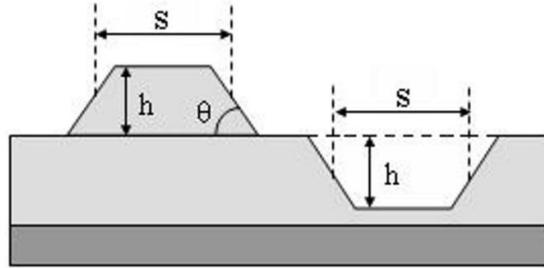

Fig.1. Schematic view of the cross section of shape assumed for dot and pit.

The total free energy to form either a dot or a pit is $E = E_S + E_R$, where E_S and E_R are the change in surface free energy and the reduction of the strain energy by elastic relaxation, respectively. Minimizing the total free energy [6] with respect to shape for fixed volume gives $s = t = h \times ctg\theta$, where s, t, h and θ are the length, width, height (depth) and contact angle, as in Fig. 1, the energy is equal to

$$E = 4\Gamma V^{2/3} \tan^{1/3}\theta - 6cV \tan\theta, \tag{1}$$

where $\Gamma = \gamma_e \csc\theta - \gamma_s \cot\theta$. . For the crystals with a cubic symmetry $\gamma_s = \frac{1}{2}\varepsilon^2(C_{11} + C_{44})d_{wet}$,

$c = \sigma_b^2 \frac{(1-\nu)}{2\pi\mu}$, $\sigma_b = \varepsilon(C_{11} + C_{44})$. Here γ_s and γ_e are the surface free energy per unit area for the

normal orientation and the beveled edge, respectively, $\varepsilon = \frac{\Delta a}{a}$ is the lattice mismatch ratio (strain)

and d_{wet} is the wetting layer thickness. $\nu = \frac{\lambda}{2(\lambda + \mu)}$ is the Poisson ratio, μ, λ and C_{ij} are the

shear (Lame) coefficients and the elastic modulus of the substrate. Taking into account also the dependence of the wetting layer thickness versus strain, the expression for the total energy can be written as

$$E = 4\left(\gamma_e \csc\theta - \frac{1}{2}\varepsilon^2 (C_{11} + C_{44}) ae^{-35.84\varepsilon} ctg\theta\right) V^{2/3} \tan^{1/3}\theta - 3\varepsilon^2 (C_{11} + C_{44})^2 \frac{(1-\nu)}{\pi\mu} V \tan\theta. \tag{2}$$

Dependence of the InAsSbP strain-induced dots and pits total energy versus volume, calculated at $\gamma_e = 5 \times 10^{-5} \text{ J/cm}^2$, $\mu = 3.537 \times 10^5 \text{ J/cm}^3$, $C_{11} = 8.267 \times 10^5 \text{ J/cm}^3$, $C_{44} = 3.9564 \times 10^5 \text{ J/cm}^3$,

$\nu = 0.361$, $d_{wet} = ae^{-35.84 \cdot \varepsilon}$ cm, $a = 152.6536 \times 10^{-8}$ cm and $\theta = 0.785$ (45°), is presented in Fig.2A for different values of the strain. To attain a stable geometry, the island must first overcome the energy barrier E^* which occurs at volume V^*. Finding the maximum of (2), dependences of the critical energy and volume versus strain are presented in Figs. 2B and 2C, respectively. From these figures we see that either E^* or V^* strongly depend on the strain and dramatically decrease at the increasing of the strain, and at the critical strain of ε* = 0.0105 the sign is changed. We assume that at ε = ε* the mechanism of the nucleation is changed from the growth of dots to the nucleation of pits. Clearly, at small misfit (ε < ε*), the bulk nucleation mechanism dominates. But at ε > ε*, when the energy barrier becomes negative as well as a larger misfit provides a low-barrier path for the formation of dislocations, the nucleation of pits becomes energetically preferable.
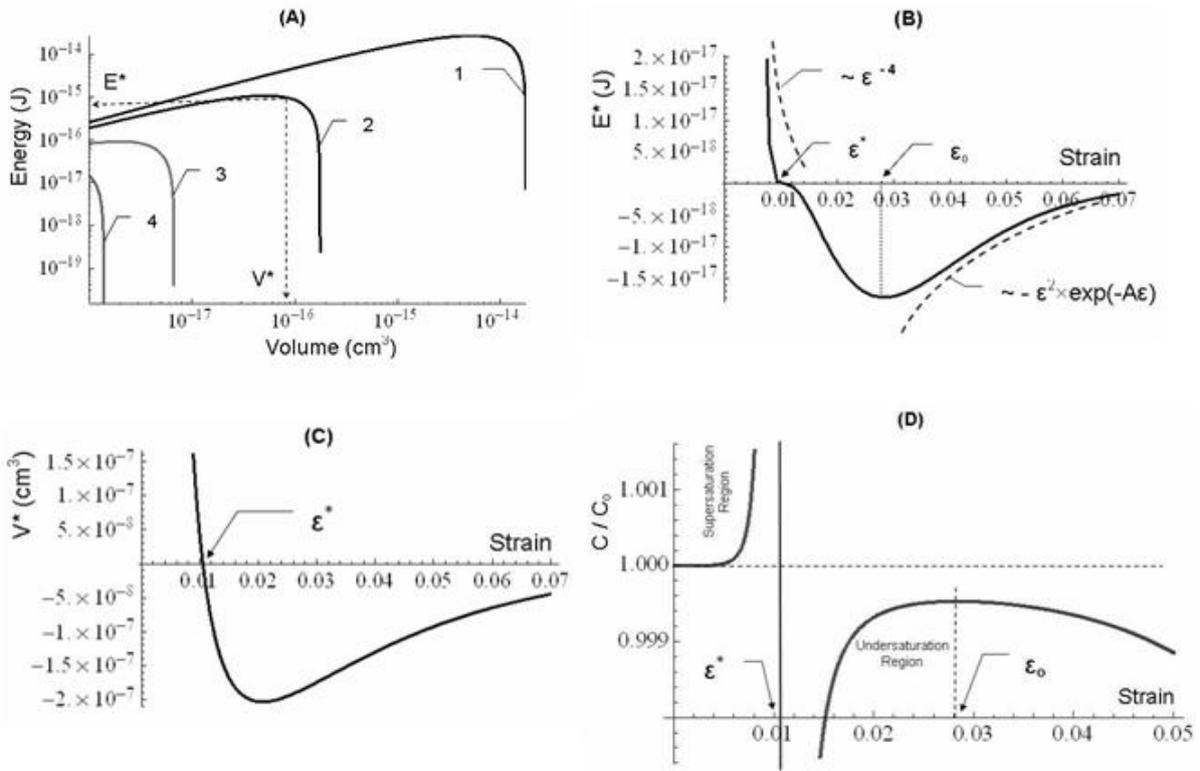

Fig.2. A – dependence of the InAsSbP strain-induced islands (dots and pits) energy versus volume at different strain (1 – ε=0.002, 2 – ε=0.004, 3 – ε=0.006, 4 – ε=0.007). B – critical energy, C – volume and D – liquid phase saturation level versus strain.

In order to certain of our assumption we employed also the atomistic model of nucleation for the InAsSbP-based strain-induced dots and pits grown by LPE. According to this model [7], the expression for the total energy can be written as

$$\Delta E_m = -n(m)\Delta\mu + q(m)\varphi, \quad (3)$$

where *m* is the number of atoms along one side of the nucleus, *q(m)* is the number of additional broken bonds, *n* is the number of atoms in the nucleus, φ is the heat of crystallization per bond (φ = 0.0434 eV for InAs) and Δμ is the difference in chemical potential. Taking into account that at

the nucleation on the (100) surface $n(m) = 2m^2$, $q(m) = 4m$ and that $\mu = \mu_o + kT \cdot LnC$, expression (3) can be written as

$$\Delta E_m = -2m^2 kTLn \frac{C}{C_o} + 4m\varphi, \tag{4}$$

where μ_0 is the chemical potential of the free element, k is the Boltzmann constant, T is absolute temperature, C_0 and C are the equilibrium and current concentrations in the liquid phase at the T_o growth temperature, respectively. Actually, C/C_o is the ratio which shows the saturation level of the liquid phase. From calculation of the maximum of (4), the critical energy can be written as

$$\Delta E^* = 2\phi^2 \bigg/ kT_o Ln \frac{C}{C_o}. \tag{5}$$

Comparing the values of critical energies for both models, the direct dependence of the liquid phase saturation level (C/C_o) versus strain (ε) is developed, which for the growth temperature of T_o=823 K is graphically presented in Fig. 2D. This function has a discontinuation at $\varepsilon = \varepsilon^*$ and at $\varepsilon < \varepsilon^*$, $C > C_o$, which means that the liquid phase is supersaturated and the growth of the island must take place. Otherwise, when $\varepsilon > \varepsilon^*$, $C < C_o$, the liquid phase is undersaturated and, as a result, the dilution of the wetting layer or the substrate is performed in the form of nucleation of the pit. Because the mixing of the atoms in InAsSbP quaternary alloy occurs between As, Sb and P atoms on the arsenic sublattice, this material system is described in mixing problem as a ternary mixture of InAs, InSb and InP compounds. It is known [8] that the free energy for the ternary compounds versus their composition and temperature is described by the following expression:

$$\begin{aligned} F(x,y,T) &= \omega_{InAs}(1-x-y) + \omega_{InSb}x + \omega_{InP}y + \alpha_{InAs-InSb}(1-x-y)x + \alpha_{InSb-InP}xy \\ &+ \alpha_{InAs-InP}(1-x-y)y + RT[(1-x-y)Ln(1-x-y) + xLn\,x + yLn\,y] \end{aligned} \tag{6}$$

where ω_i - are the sum of the first and second nearest neighbor interaction energies (i.e., internal energies) for binary component compounds, α_i are the pseudobinary interaction parameters, T is the absolute temperature and R is the gas constant. The results and schematic view of the free energy calculations based on the strictly regular solution approximation, for our ternary and quaternary materials are presented in Fig.3 (A-D) and Fig.4(A), respectively, at the temperature region of $T = 573$–973K. In contrary to InAs-InSb and InAs-InP compounds, for the InSb-InP system the immiscibility gap occurs, as it is seen from Fig.3(C). The binodal and spinodal regions concentration edges dependence on the temperature are presented in Fig.3(D).

The concentration equilateral triangle for the InAsSbP material system is presented in Fig.4(B). By the dotted ovals are presented the corresponding concentration regions, where the positive or negative sign of misfit are reached. The calculations data are presented in the inserted table.
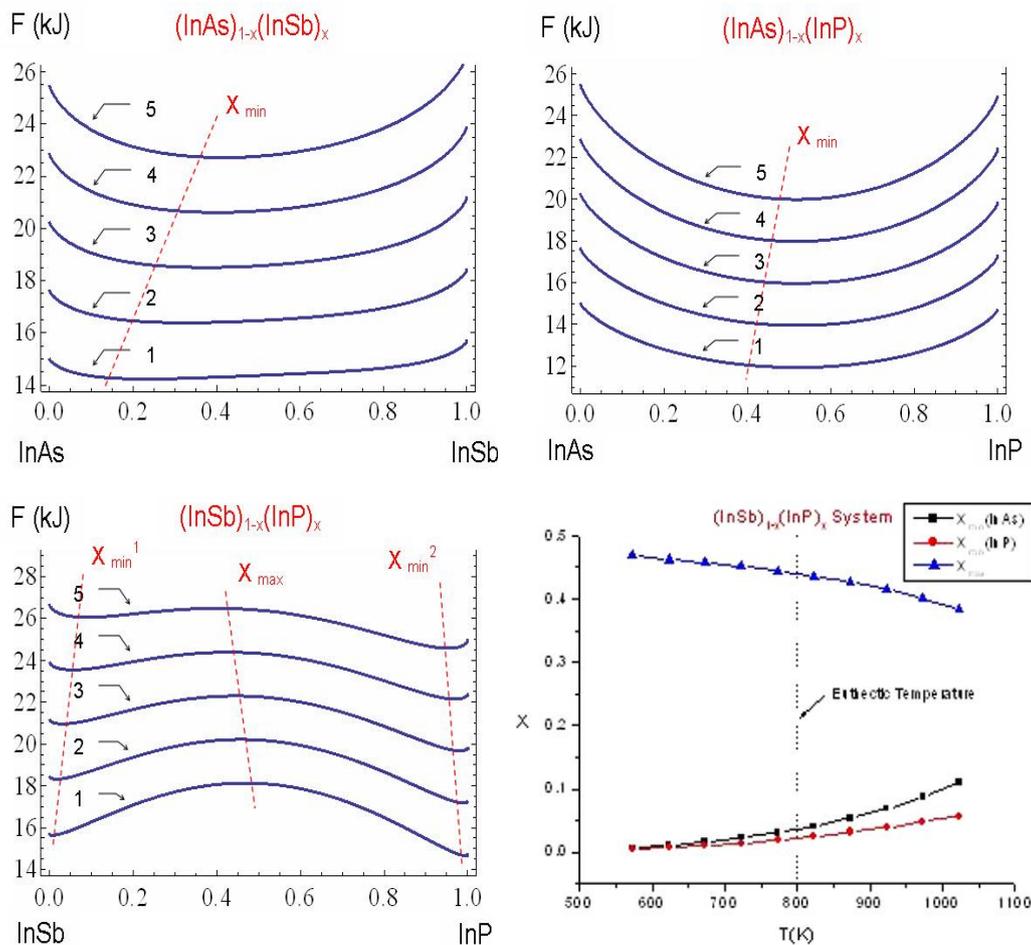
Fig.3. Dependence of the InAs-InSb (A), InAs-InP (B) and InSb-InP (C) ternary compounds free energy versus concentration at: 1 – T=573K, 2 – T=673K, 3 – T=773K, 4 – T=873K, 5 – T=973K. (D) – Dependence of the binodal and spinodal concentration regions versus temperature for InSb-InP system.
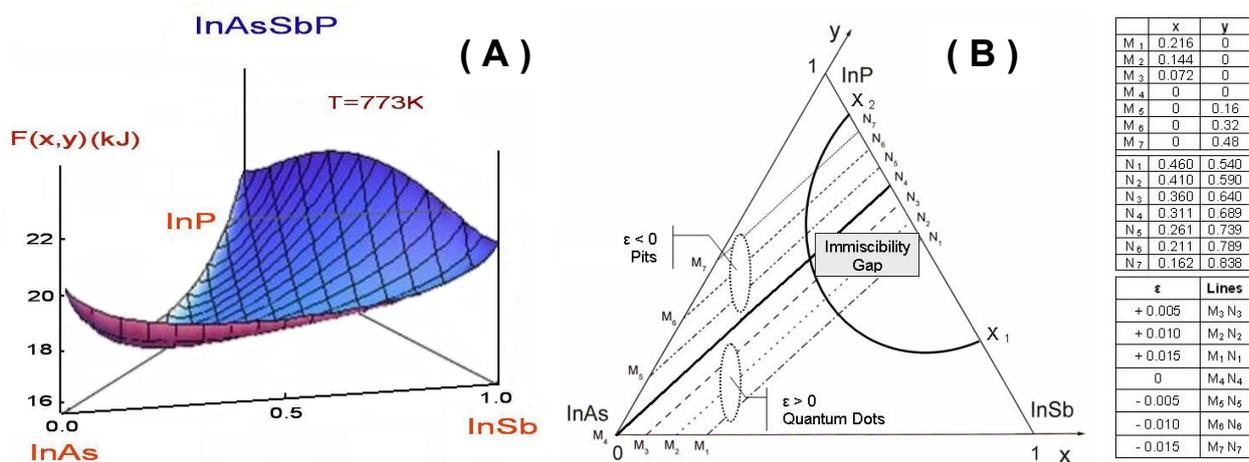

Fig.4. A schematic view of the free energy (A) and the concentration equilateral triangle (B) for the InAsSbP material system. Region denoted by solid curve corresponds to immiscibility gap at T=500°C.

4. Conclusions

Thus, the energetic task and dots–pits competing nucleation mechanisms in strain-induced InAsSbP system are discussed. The critical strain when the mechanism of nucleation is changed

from the growth of dots to the nucleation of pits is calculated. The concentration regions for the growth of InAsSbP quaternary dots and pits are denoted.

References

1. K. Nishi, H. Saito, S. Sugou, and J.S. Lee. Appl. Phys. Lett., 74, 1111 (1999).

2. D. Haft, R.J. Warburton, K. Karrai, et al. Appl. Phys. Lett., 78, 2946 (2001).

3. K.M. Gambaryan, V.M. Aroutiounian, et al. J. Phys. D: Appl. Phys., 41, 162004 (2008).

4. I. Stranski and L. Krastanow. Math.-Naturwiss., 146, 797 (1938).

5. Z. Gong, Z. Fang, Z. Miao, and Z. Niu. International Journal of Nanoscience, 5, 883 (2006).

6. J. Tersoff and F.K. LeGoues. Phys. Rev. Letters, 72, 3570 (1994).

7. A. Kramer, T. Boeck, P. Schramm, and R. Fornari. Physica E, 40, 2462 (2008).

8. K. Onabe. NEC Res. & Develop., 72, 1 (1984).