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Growth features and nucleation mechanism of $Ga_{1\text{-}x\text{-}y}In_xAl_yN$ material system on GaN substrate

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Abstract. The continuum elasticity model is applied to investigate quantitatively the growth features and nucleation mechanism of quantum dots, nanopits, and joint QDs–nanopits structures in GaInAlN quasyternary systems. We have shown that for GaInAlN material system at the critical strain of $\varepsilon^* = 0.039$ the sign of critical energy and volume is changed. We assume that at $\varepsilon = \varepsilon^*$ the mechanism of the nucleation is changed from the growth of quantum dots to the nucleation of nanopits. Obviously, at small misfit ($\varepsilon < \varepsilon^*$), the bulk nucleation mechanism dominates. However, at $\varepsilon > \varepsilon^*$, 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. The free energy of mixing for $Ga_{1-x-y}In_xAl_yN$ quasiternary system was calculated and studied and its 3D sketch was plotted.

Keywords: quantum dot; nanopit; strain energy; Gibbs free energy; immiscibility gap

1. Introduction

The most promising from the point of view of designing new materials and devices with unique properties is at present elaboration of technologies for creation of novel semiconductor nanostructures and study of their physical properties. Steadily increasing interest towards specifically semiconductor nanostructures is caused primarily by the existence of a wide spectrum of possibilities to control the properties of semiconductors. It is known that crucial changes in their properties may be achieved by varying the composition of semiconductor solid solutions, changing the concentration and type of impurities, changing external conditions and so on. Constraints of motion of charge carriers in one or more directions leading to the dimensional quantization phenomenon open additional possibilities of efficient control of properties of nanostructure-based devices by means of changing their sizes (Tersoff and Le Goues 1994, Gambaryan 2010, Gambaryan *et al.* 2011, Aroutiounian *et al.* 2010). Modified density of states of quantum dots (QDs), nanowires, and combined QD-nanopit structures leads to essential improvement of the working optoelectronic parameters of semiconductor devices, such as lasers, photodetectors, etc. Obviously, the electronic properties of QDs depend on dot structure and the mechanism of their

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formation. Such nanostructures can be fabricated by nanolithography or by the self-organization method (Stranski–Krastanov mode), which at present is the most frequently employed technique. Relaxation of elastic (deformation) strain as a principle of nucleation is the basic mechanism of formation of nanostructures in semiconductor materials such as Si, Ge, III–V compounds, etc.

GaN, InN, AlN and their ternary and quaternary alloys are considered as one of the important semiconductors. There are fabricated lighting and displayed application on the base of those materials (Ihsiu and Stringfellow 1996). Particularly, GaInN alloys have recently attracted much attention as potential materials for fabrication of blue and green light-emitted diodes (LEDs), as well as for violet and blue injection lasers (Nakamura *et al.* 1995). Since the band gap of GaInN can be varied from 2.0 to 3.5 eV by increasing GaN concentration, the potential operating wavelengths cover nearly the entire visible spectra range (Nakamura *et al.* 1996). GaN is a promising material for use it in high-speed field effect transistors, high-temperature electronic devices, UV or blue light emitters, detectors and gas sensors (Kim *et al.* 2010). It is known that InN has lowest effective mass and small band gap among all III-nitride semiconductors, which can allow suggesting that it can be used in light-emitting devices and high-speed electronic devices as well. In particular, by controlling indium composition, InN-related compounds, including $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$, have been used for band-gap engineering, which have extended the emission of nitride-based light-emitting diodes from the UV to near-infrared regions. InN can also be used in tandem solar cells and thermophotovoltaic systems (Kim *et al.* 2010). In addition, the sufficient lattice mismatch between GaN/AlN, GaN/InN and InN/AlN equals to 3%, 10% and 12% respectively, allows considering those materials as very attractive also for nanostructures engineering in Stranski–Krastanov growth mode.

Regarding the research and development of III-nitride QDs, there are three main kinds of formation mechanism for the growth of QDs. First, it has been proposed (Lozano *et al.* 2005, 2007) that nanoscale indium composition fluctuation due to InGaN phase separation or indium segregation results in the formation of indium-rich clusters, which acts as QDs (QDs-like). Hence, QDs-like system acts as an extremely sophisticated quantum capture system, and in QDs, the charge carriers are deeply localized so as to hinder their migration toward nonradiative defects (dislocations). Therefore, high luminescence efficiency could be expected if the density of QDs is much higher than that of dislocations. Second, it has been shown that nitride QDs can be self-organized using the strain-induced Stranski-Krastanov growth mode (Bi *et al.* 2014, Soto Rodriguez *et al.* 2013). Third, another way to form nitride QDs is to take advantage of surfactants or antisurfactants, which are often used to change the surface free energy of heterostructure interface. However, the self-assembled nitride QDs can be fabricated by molecular-beam epitaxy or by metalorganic chemical vapor deposition (Lozano *et al.* 2007, Bi *et al.* 2014, Soto Rodriguez *et al.* 2013) without using any antisurfactants. High-density GaN/AlN QDs for deep UV LED with high quantum efficiency (Lahourcade *et al.* 2009, Yang *et al.* 2014) have been also successfully grown by molecular beam epitaxy.

In the present report, the continuum elasticity model is applied to investigate quantitatively the growth features and nucleation mechanism of QDs, nanopits, and cooperative QDs–nanopits structures in GaInAlN quasiternary material system.

2. Calculation of total energy of cooperative QD-nanopit structures in GaInAlN material system

At the description of the competing nucleation mechanism, we assume that the surface has only

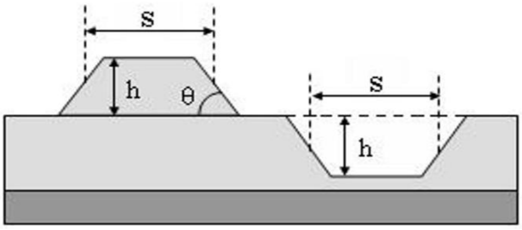


Fig. 1 Schematic view of the QD-nanopit structure's cross section

discrete orientations and that only one angle needs to be considered (Tersoff and Tromp 1993), so GaInAlN-based QDs and nanopits have a shape as it is schematically presented in Fig. 1.

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 (Tersoff and Tromp 1993) with respect to shape for fixed volume gives $s = t = h\times\cot\theta$, 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 $\gamma_s = \frac{1}{2}\cdot\varepsilon^2(C_{11}+C_{44})d_{wet}$, $c = \sigma_b^2\frac{(1-\nu)}{2\pi\mu}$, $\sigma_b = \varepsilon(C_{11}+C_{44})$. 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. The value for γ_e can be found from Young equation $\gamma_{sl} = \gamma_s - \gamma_e\cos\theta$ (Żenkiewicz 2007), where for Stranski–Krastanov growth mode $\gamma_{sl} = 0$ is the surface free energy corresponding to the solid-liquid interface, $\nu = \frac{\lambda}{2(\lambda+\mu)}$ 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 dependence of the wetting layer thickness versus strain, the expression for the total energy can be written as

$$\begin{aligned} E = {} & 4\left(\gamma_e Csc\theta - \frac{1}{2}\varepsilon^2(C_{11}+C_{44})a\cdot e^{-35.84\varepsilon}\cot\theta\right)V^{2/3}\tan^{1/3}\theta \\ & -3\varepsilon^2(C_{11}+C_{44})^2\cdot\frac{(1-\nu)}{\pi\mu}\cdot V\tan\theta \end{aligned} \tag{2}$$

In order to obtain analytical expression for the strain (deformation) dependence of wetting layer thickness in the case of the GaInAlN quasiternary system, we performed mathematical approximation of experimental data. Approximation curves are presented in Fig. 2. We used in our calculations the following expressions for d_{wet} in monolayers (ML): (i) if the deformation strain is positive, then $d_{wet} = 0.05\varepsilon^{-3/2}$ at $\varepsilon > 0.03$ (Biehl *et al.* 2005) and $d_{wet} = 24.181e^{-31.034\varepsilon}$ at

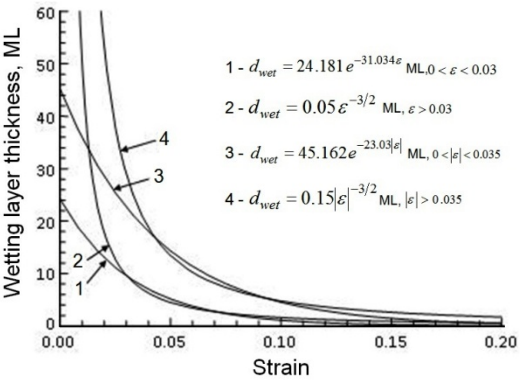
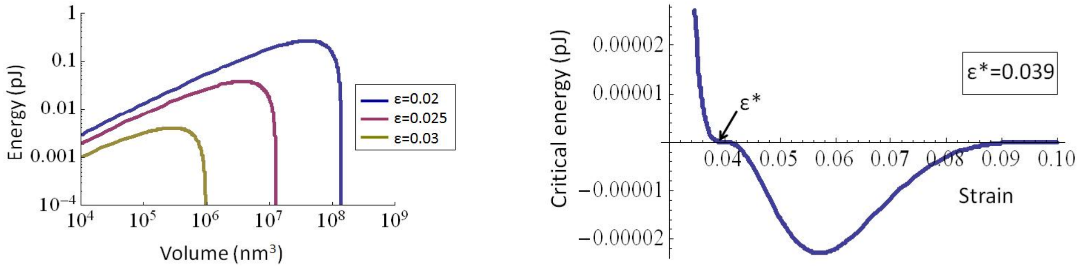


Fig. 2 Strain-dependence of the wetting layer thickness

$0 < \varepsilon < 0.03$ (accuracy of approximation R^2 = 0.9635); (ii) if the deformation strain is negative, then $d_{wet} = 0.15|\varepsilon|^{-3/2}$ at $|\varepsilon| > 0.035$ (Biehl *et al.* 2005) and $d_{wet} = 45.162e^{-23.03|\varepsilon|}$ at $0 < |\varepsilon| < 0.035$ (accuracy of approximation R^2 = 0.9934).

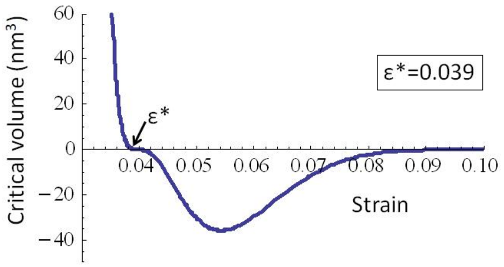
Dependence of the GaInAlN strain-induced dots and pits total energy versus volume, calculated at $\gamma_e = 10.15 \cdot 10^{-5}$ J/cm^2, $\mu = 30.34 \cdot 10^4$ J/cm^3, $C_{11} = 272.3 \cdot 10^3$ J/cm^3, $C_{44} = 130.3 \cdot 10^3$ J/cm^3, $\nu = 0.361$ and $\theta = 0.785$ (45°), is presented in Fig. 3(a) at different values of strain.

In order 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 critical volume versus strain are presented in Figs. 3(b) and (c), respectively. From those figures is quite visible that both E^* and V^* strongly depend on the strain and dramatically decrease at the



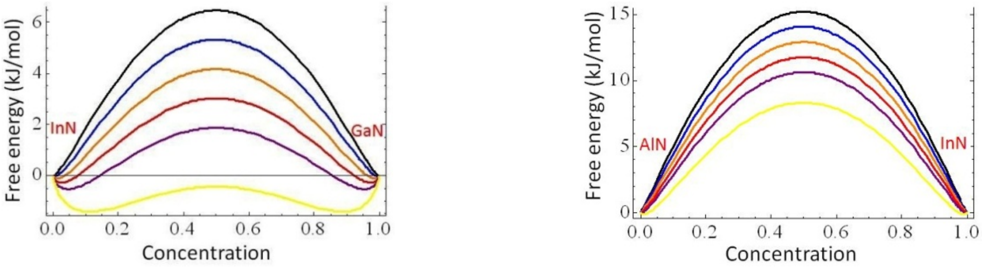
(a) Energy versus nanostructure's volume

(b) Critical energy versus strain

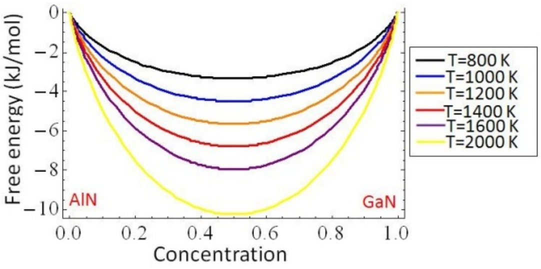


(c) Critical energy versus strain

Fig. 3 Dependence of the GaInAlN strain-induced islands (dots and pits) energy versus nanostructure's volume at different strain – (a) Critical energy and critical volume versus strain – (b, c)



(a) GaInN (b) InAlN



(c) GaAlN

Fig. 4 Concentration dependence of the compounds molar free energy

increasing of the strain, and at the critical strain of $\varepsilon^* = 0.039$ the sign of energy and volume is changed. We assume that at $\varepsilon = \varepsilon^*$ the mechanism of the nucleation is changed from the growth of dots to the nucleation of pits.

Clearly, at small misfit ($\varepsilon < \varepsilon^*$), the bulk nucleation mechanism dominates. However, at $\varepsilon > \varepsilon^*$, 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.

Next, we calculated the free energy of mixing of the $Ga_{1-x-y}In_xAl_yN$ quasiternary systems using the following relationship

$$\Delta G(x, y) = \Delta H - T\Delta S, \tag{3}$$

where T is the absolute temperature, ΔH and ΔS are, respectively, the enthalpy and entropy of mixing which are determined by the following expressions (Ihsiu and Stringfellow 1996, Emeljanova *et al*. 2009, Deibuk 2003, Vigdorovich and Sveshnikov 2000)

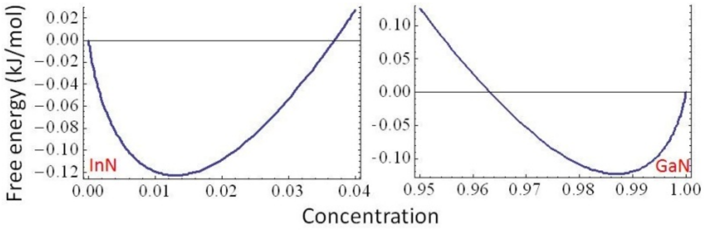
$$\begin{gathered} \Delta H(x,y) = \alpha_{GaN-InN}(1-x-y)x + \alpha_{InN-AlN}xy + \alpha_{GaN-AlN}(1-x-y)y \\ \Delta S(x,y) = RT\{x\ln x + y\ln y + (1-x-y)\ln(1-x-y). \end{gathered} \tag{4}$$

Here α is the parameter of pseudobinary interaction, and R the universal gas constant (Ihsiu and Stringfellow 1996, Vigdorovich and Sveshnikov 2000). The interaction parameter α is the characteristic index of immiscibility tension. According to the model of "delta-lattice parameter" (DLP), the interaction parameter is represented in the form

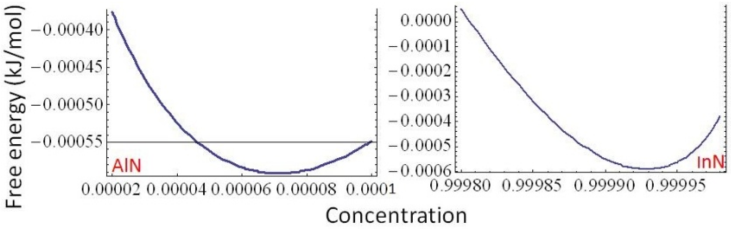
$$\alpha_{AB} = 4k\left[\frac{1}{2}(a_A^{-2.5} + a_B^{-2.5}) - \left(\frac{(a_A + a_B)}{2}\right)^{-2.5}\right], \tag{5}$$

where a_A and a_B are the lattice constants of A and B components and k is a constant. For compounds with cubic symmetry and at relatively small mismatch between the lattice parameters, the factor k is taken to be equal to 1.15×10^7 cal/(mole×Å$^{2.5}$) (Vigdorovich and Sveshnikov 2000, Wakahara *et al*. 1997, Stringfellow 1999). Therefore, we used this value of k only for the GaInAlN system.

Concentration dependences of the free energy per mole for the GaInN, GaAlN, and InAlN systems at different temperatures in the range of 800-2000 K are shown in Fig. 6. For construction of those plots, Eq. (3) was used with ΔH and ΔS taken from Eq. (6).

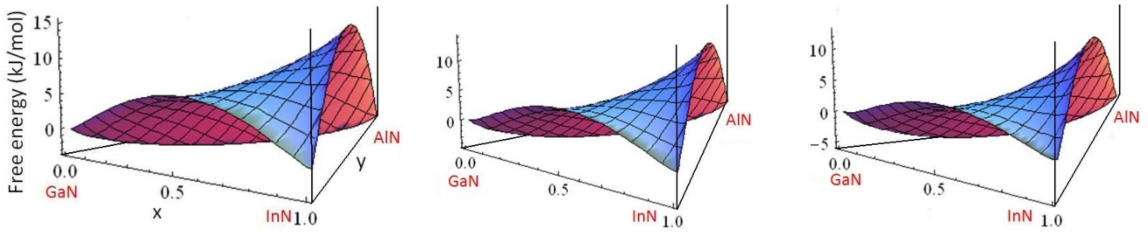


(a) GaInN compound

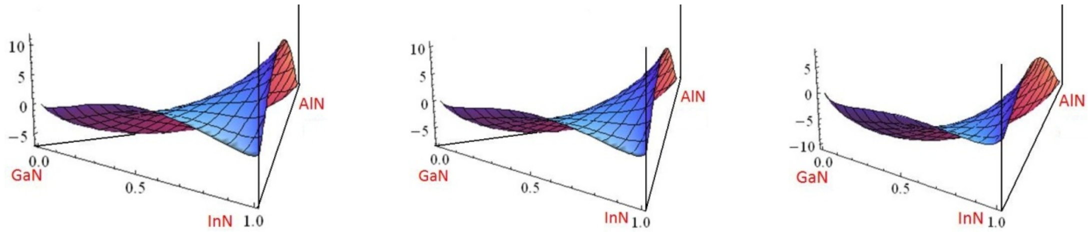


(b) InAlN compound

Fig. 5 Binodal points (magnified near the minima) of curves of molar free energy shown in Fig. 4

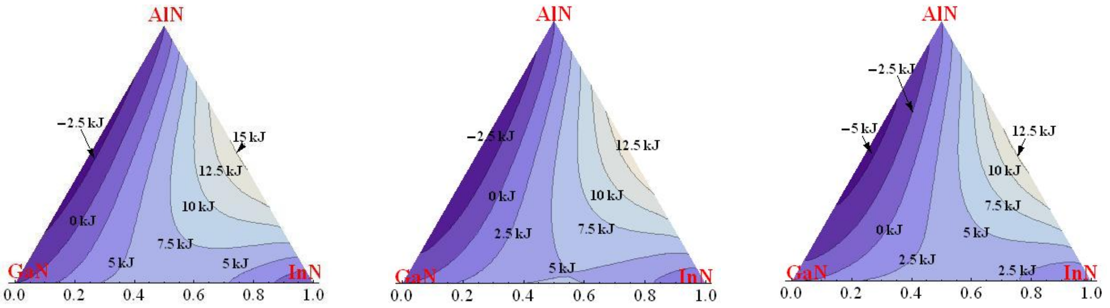


(a) $T = 800$ K (b) $T = 1000$ K (c) $T = 1200$ K

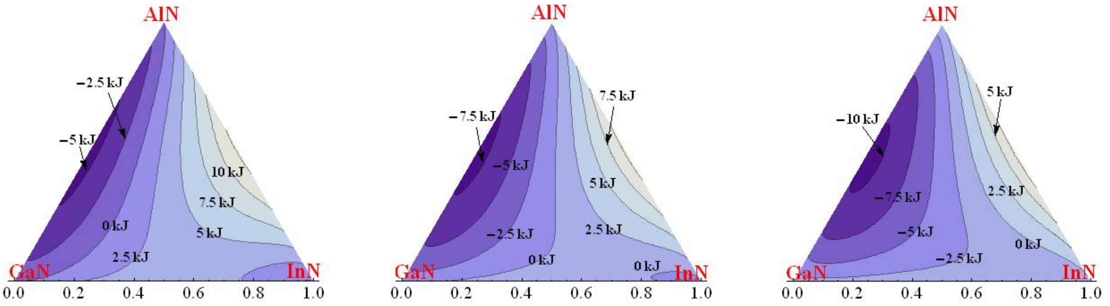


(d) $T = 1400$ K (e) $T = 1600$ K (f) $T = 2000$ K

Fig. 6 Schematic 3D pattern of the molar free energy of the GaInAlN material system



(a) $T = 800$ K (b) $T = 1000$ K (c) $T = 1200$ K



(d) $T = 1400$ K (e) $T = 1600$ K (f) $T = 2000$ K

Fig. 7 Isoenergic sections of the molar free energy of the GaInAlN quasiternary system at the temperatures (a-f) 800-2000 K, respectively

It is seen in Fig. 4 that as distinct from AlN-GaN, in the InN-GaN and AlN-InN systems a region of immiscibility appears, which is caused by an increase in free energy at the increase of gallium concentration into InN and indium concentration into AlN. In systems with large difference in lattice constants, high positive enthalpy of mixing can overcome the negative entropy of mixing at temperatures below critical, leading to an increase in free energy. This means that in equilibrium a disordered solid solution with a composition between the binodal points shown in Fig. 5 will decay into two separate solid phases (Stringfellow 1999).

However, as it is seen from Fig. 5, narrow miscibility gaps exist for InGaN and AlInN material systems, but at very low (impurity level) concentrations.

Schematic 3D patterns of molar free energy depending on composition of the GaInAlN quasiternary system at 800-2000 K temperatures and corresponding iso-energetic sections are presented in Figs. 6 and 7, respectively.

3. Conclusions

Thus, the continuum elasticity model was applied to investigate quantitatively the growth features and nucleation mechanism of QDs, nanopits and cooperative QDs–nanopits structures in GaInAlN quasiternary systems. It was shown, that nanostructures formation critical energy (E^*) and critical volume (V^*) strongly depend on the strain and dramatically decrease at the increasing of the strain. Calculations revealed that for GaInAlN material system at the critical strain of $\varepsilon^* = 0.039$ the sign of critical energy and volume is changed. At $\varepsilon = \varepsilon^*$ the mechanism of the nucleation is changed from the growth of QDs to the nucleation of nanopits. At small misfit ($\varepsilon < \varepsilon^*$), the bulk nucleation mechanism dominates. However, at $\varepsilon > \varepsilon^*$, 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. Presented results are very important from technological point of view and can be used at nanoengineering in GaInAlN material system.

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