GaInAlN material system: nanostructures growth features and immiscibility analysis

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ABSTRACT

The continuum elasticity model is applied to quantitatively investigate the growth features and nucleation mechanism of quantum dots (QDs), nanopits, and joint QDs–nanopits structures in GaInAlN quasyternary systems. We have show 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 Gibbs free energy of mixing of mixing for $Ga_{1-x-y}In_xAl_yN$ quasiternary system was calculated and studied and its 3D sketch plotted. It was demonstrated that there is an immiscibility gap for that system, which strongly depends on temperature.

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 1994, Gambaryan 2010 2011, Aroutiounian 2010). Modified density of states of quantum dots (QD), nanowires, and combined QD-nanopit structures leads to essential improvement of the working optoelectronic parameters of semiconductor devices, such as lasers,

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photodetectors, etc. Obviously, the electronic properties of QDs depend on dot structure and the mechanism of their formation. Such nanostructures can be fabricated by nanolithography or by the self-organization method (Stranski–Krastanov mode), which is at present 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 ternaries and quaternaries alloys are considered as one of the important semiconductors. There are fabricated lighting and displayed application on the base of those materials (Ihsiu 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 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 1996, Strite 1995). 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 2010). It is known that InN has lowest effective mass and small band gap among all III-nitride semiconductors, which can allow to suggest 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 also can be used in tandem solar cells and thermophotovoltaic systems (Kim 2010). In addition, the sufficient lattice mismatch between GaN/AlN, GaN/InN and InN/AlN equals to 3%, 10% and 12% respectively, allows to consider those materials as very attractive also for nanostructures engineering in Stranski–Krastanov growth mode.

In this paper, the continuum elasticity model is applied to quantitatively investigate the growth features and nucleation mechanism of QDs, nanopits, and cooperative QDs–nanopits structures in GaInAlN quasiternary systems. The Gibbs Gibbs free energy of mixing of mixing for the GaInAlN quasiternary system is also calculated and studied.

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 discrete orientations and that only one angle needs to be considered (Tersoff 1993), and that QDs and pits have a shape schematically presented in Fig.1.
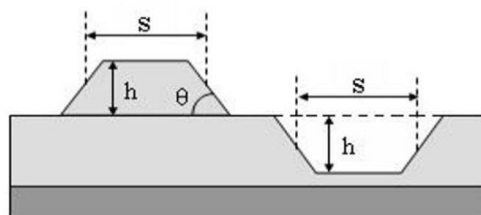

Fig. 1 Schematic view of the QD-nanopit structure's cross section

The total Gibbs free energy of mixing 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 Gibbs free energy of mixing and the reduction of the strain energy by elastic relaxation, respectively. Minimizing the total Gibbs free energy of mixing (Tersoff 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

$$E = 4\Gamma V^{2/3} \text{Tan}^{1/3}\theta - 6cV\text{Tan}\theta, \qquad (1)$$

where $\Gamma = \gamma_e \text{Csc}\theta - \gamma_s \text{Cot}\theta$. For the crystals with a cubic symmetry $\gamma_s = \frac{1}{2} \cdot \varepsilon^2 (C_{11} + C_{44}) d_{\text{wet}}$, $c = \sigma_b^2 \frac{(1-\nu)}{2\pi\mu}$, $\sigma_b = \varepsilon(C_{11} + C_{44})$. Here γ_s and γ_e are the surface Gibbs free energy of mixing 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 $\gamma_{sl} = \gamma_s - \gamma_e \text{Cos}\theta$ (Żenkiewicz 2007), where for Stranski–Krastanov growth mode $\gamma_{sl} = 0$ is the surface Gibbs free energy of mixing 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

$$E = 4\left(\gamma_e \text{Csc}\theta - \frac{1}{2}\varepsilon^2 (C_{11} + C_{44})a \cdot e^{-35.84\varepsilon}\text{Cot}\theta\right)V^{2/3}\text{Tan}^{1/3}\theta -$$
$$- 3\varepsilon^2 (C_{11} + C_{44})^2 \cdot \frac{(1-\nu)}{\pi\mu} \cdot V\text{Tan}\theta \qquad (2)$$

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 $d_{\text{wet}} = 0.05\varepsilon^{-3/2}$ at $\varepsilon > 0.03$ (Biehl 2005) and $d_{wet} = 24.181e^{-31.034\varepsilon}$ at $0 < \varepsilon < 0.03$ (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 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 $\gamma_e = 10.15 \cdot 10^{-5} \text{ J/cm}^2$, $\mu = 30.34 \cdot 10^4 \text{ J/cm}^3$, $C_{11} = 272.3 \cdot 10^3 \text{ J/cm}^3$, $C_{44} = 130.3 \cdot 10^3 \text{ J/cm}^3$, $\nu = 0.361$ and $\theta = 0.785 \ (45^\circ)$, is presented in Fig. 3(a) at different strains.

To attain a stable geometry, the island must first overcome the energy barrier E^* which occurs at volume V^*. Finding the maximum of Eq. (2), dependences of the critical energy and critical volume versus strain are presented in Figs. 3(b) and 3(c), respectively. From those figures is quite visible that both E^* and V^* strongly depend on the strain and dramatically decrease at the 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.
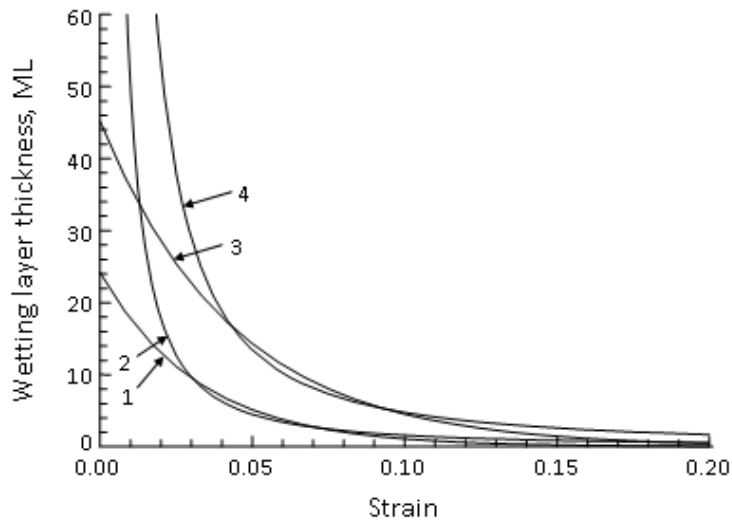

Fig. 2 Strain-dependence of the wetting layer thickness: (1) $d_{wet} = 24.181 e^{-31.034\varepsilon}$ ML, $\varepsilon > 0$; (2) $d_{wet} = 0.05\varepsilon^{-3/2}$ ML, $\varepsilon > 0$; (3) $d_{wet} = 45.162 e^{-23.03|\varepsilon|}$ ML, $\varepsilon < 0$; (4) $d_{wet} = 0.15|\varepsilon|^{-3/2}$ ML, $\varepsilon < 0$.
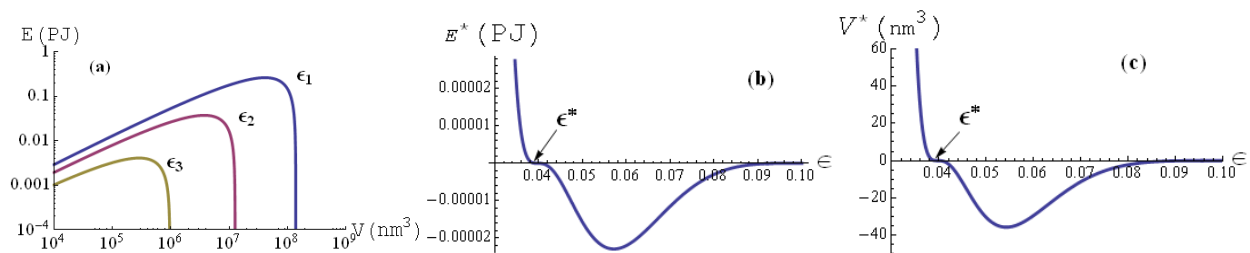

Fig. 3 (a) – dependence of the GaInAlN strain-induced islands (dots and pits) energy versus nanostructure's volume at different strain (1 – ε_1=0.02, 2 – ε_2=0.025, 3 – ε_3=0.03). Critical energy – (b) and critical volume – (c) versus strain

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.

3. THE GIBBS FREE ENERGY OF MIXING OF THE GaInAlN MATERIAL SYSTEM

Next, we calculated the Gibbs 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 and ΔH and ΔS are, respectively, the enthalpy and entropy of mixing which are determined by the following expressions (Ihsiu 1996, Emeljanova 2009, Deibuk 2006, Vigdorovich 2000):

$$\Delta H(x, y) = \alpha_{GaN-InN}(1 - x - y)x + \alpha_{InN-AlN}xy + \alpha_{GaN-AlN}(1 - x - y)y \tag{4}$$

$$\Delta S(x, y) = RT\{x \ln x + y \ln y + (1 - x - y)\ln(1 - x - y)$$

Here α is the parameter of pseudobinary interaction, and R the universal gas constant (Ihsiu 1996, Vigdorovich 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 of lattice parameters, the factor k is taken to be equal to 1.15×10^7 cal/(mole×Å$^{2.5}$), (Vigdorovich 2000, Wakahara 1997, Stringfellow 1999). Therefore, we used this value of k for the GaInAlN system only at relatively small mismatches.

Concentration dependences of the Gibbs free energy of mixing per mole for the GaInN, GaAlN and InAlN ternary systems at different temperatures in the range 800–2000 K are shown in Fig. 4. For the construction of these plots, Eq. (3) was used with ΔH and ΔS from Eq. (4).

It is seen from 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 Gibbs free energy of mixing at the increase in indium and aluminum concentration in the solid solution. 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 Gibbs free energy of mixing. This means that in equilibrium disordered solid solutions with compositions between the binodal points, shown in Fig. 5, will decay into two separate solid phases (Stringfellow 1999).
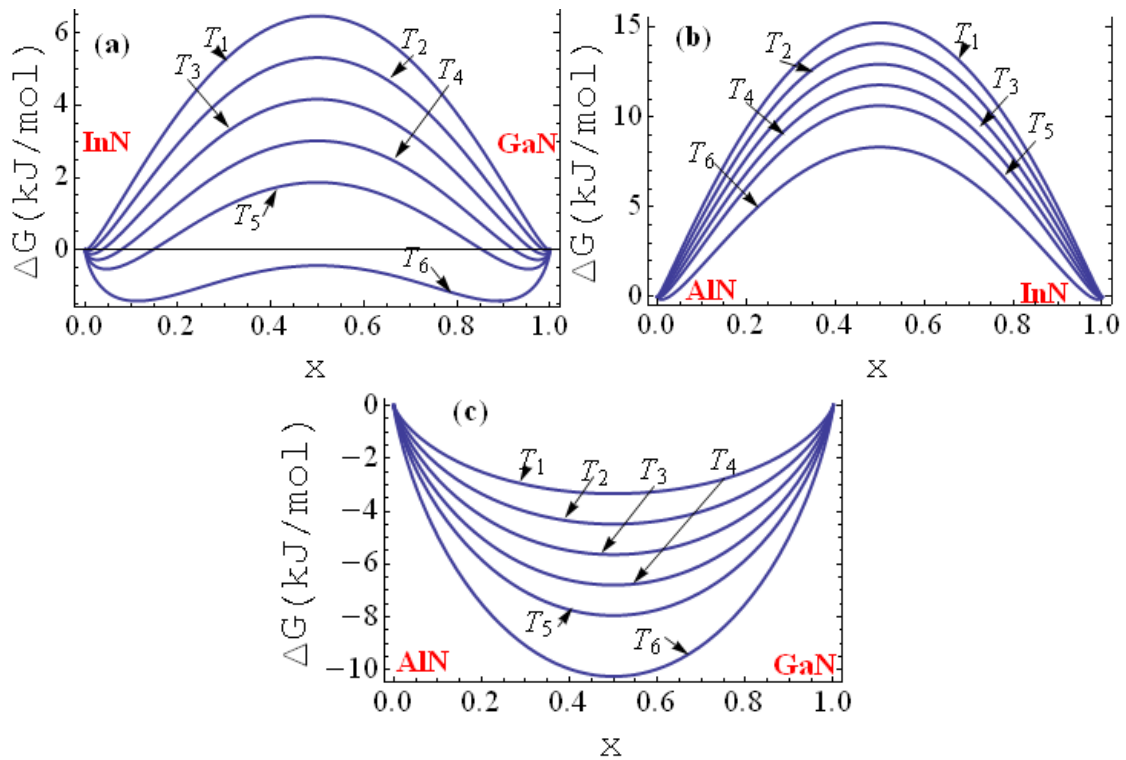
Fig. 4 Concentration dependence of the Gibbs free energy of mixing for one mole of ternary compounds GaInN (a), InAlN (b), and GaAlN (c) at temperatures (T_1) 800 K, (T_2) 1000 K, (T_3) 1200 K, (T_4) 1400 K, (T_5) 1600 K and (T_6) 2000 K
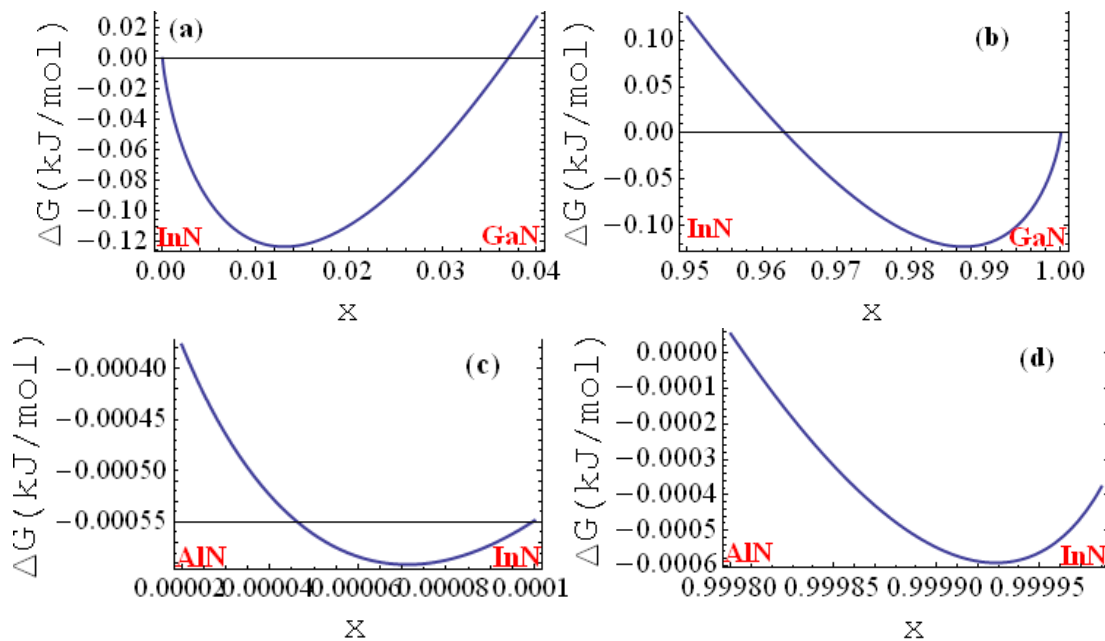

Fig. 5 Binodal points (magnified near the minima) of the molar Gibbs free energy of mixing for the systems GaInN – (a, b) (T=1200 K) and InAlN – (c, d) (T=1000 K)
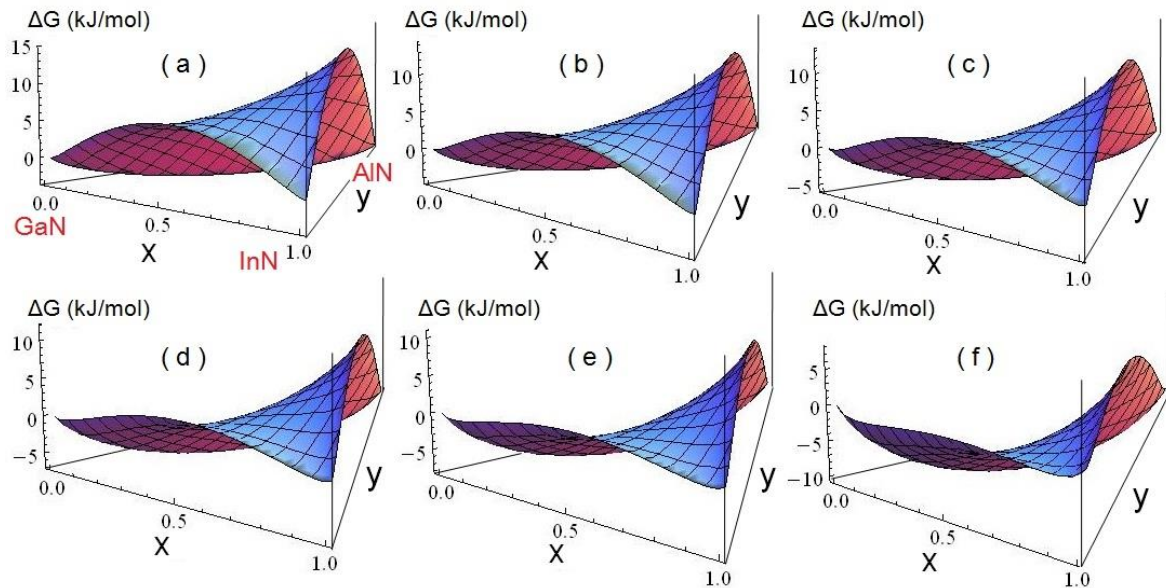
Fig. 6 3D patterns of the molar Gibbs free energy of mixing of the GaInAlN quasiternary system at (a)-800 K, (b)-1000 K, (c)-1200 K, (d)-1400 K, (e)-1600 K and (f)-2000 K
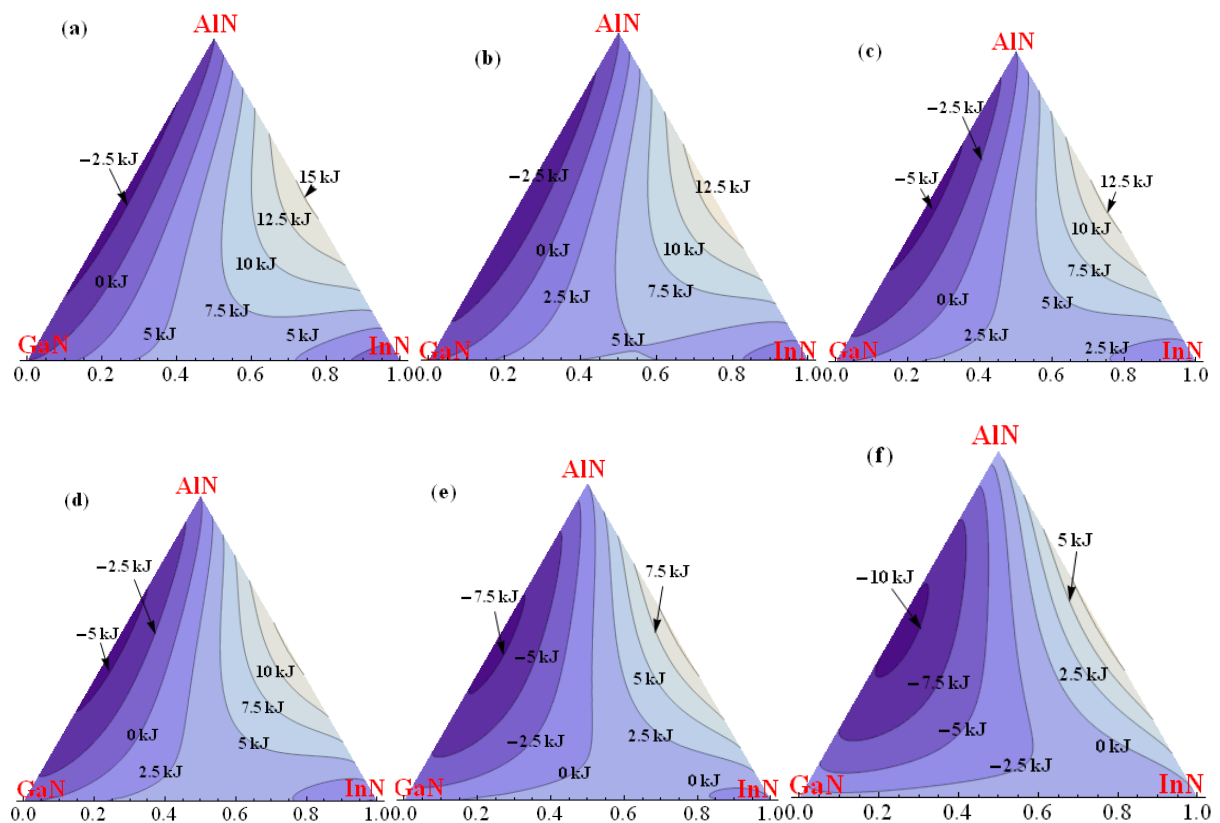

Fig. 7 Iso-energetic sections of the molar Gibbs free energy of mixing of the GaInAlN system at (a)-800 K, (b)-1000 K, (c)-1200 K, (d)-1400 K, (e)-1600 K and (f)-2000 K

Schematic 3D patterns of molar Gibbs free energy of mixing depending on composition of the GaInAlN quasiternary system at 800-2000 K and corresponding isoenergic sections are presented in Figs. 6 and 7, respectively. Actually, our calculations show (Fig. 4 and Fig. 5) that there is no immiscibility gap in GaN-AlN material system. In spite of that system, for the GaN–InN, an incorporation of components is energetically favorable only up to around 1mol.%, after that the immiscibility occurs. For the InN–AlN material system the situation is more dramatically. Here, mutual incorporation of components is energetically favorable only up to impurity levels (Fig. 5(c. d)). However, evidently the immiscibility gaps for both GaN–InN and InN–AlN solid solutions decrease at temperature increasing.

4. CONCLUSIONS

Thus, the continuum elasticity model was applied to quantitatively investigate 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. 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 Gibbs free energy of mixing for the GaAsSbP quasiternary system has been calculated and studied. It was demonstrated that there is no immiscibility gap in GaN-AlN material system. For the GaN–InN, an incorporation of components is energetically favorable only up to around 1mol.%, after that the immiscibility occurs. For the InN–AlN material system, the mutual incorporation of components is energetically favorable only up to impurity levels. Our results show that immiscibility gaps for both GaN–InN and InN–AlN solid solutions decrease at temperature increasing. Presented results are very important from technological point of view and can be used not only at nanoengineering in GaInAlN material system, but also at the growth of bulk crystals and epitaxial thin films.

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