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Nanostructures Nucleation Features and Miscibility Analysis in Zinc-Blend and Wurtzite GaN-InN-AlN Material System

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ABSTRACT

The growth mechanism of quantum dots (QDs) and nanopits in GaN-InN-AlN material system for both zinc-blend and wurtzite structures is theoretically investigated. The continuum elasticity model is used for calculations. The nanostructures energy versus their volume, as well as the critical energy and critical volume versus the QD and wetting layer lattice constants relative mismatch ratio (strain ϵ), are calculated. It was shown that when the zinc-blend GaN is used as a substrate and when the strain between the wetting layer and a substrate overcomes critical $\epsilon^*=0.039$ value, instead of QDs nucleation, the formation of nanopits becomes energetically preferable. Otherwise, when wurtzite GaN is used as a substrate the critical strain is equal to $\epsilon^*=0.01$, i.e. almost four times smaller. Miscibility gap analysis for GaInAlN quaternary material system is performed by the Gibbs free energy calculations. It is shown that immiscibility gap strongly depends not only on temperature, but also on crystallographic structure. Presented results can be useful at QDs engineering, as well as at the growth of multicomponent bulk crystals and epitaxial thin films in GaInAlN material system.

1. Introduction

The quantum dots (QDs) and other nanostructures, along with the choosing of corresponding advanced semiconducting materials and their band gap engineering, open up entirely new functionalities of traditional devices as well as new challenges for the fabrication of devices with unique properties. In particular, single photon sources for quantum cryptography, QD lasers, single photon detectors, single electron transistors, resonant tunneling diodes, etc [1-4]. Indeed, the physical properties of QDs depend on QDs size and shape, as well as on the mechanism of their formation. The most useful approach for the fabrication of QDs is Stranski-Krastanov [5] growth mode, where the sum of the surface free energy and the interface free energy is about the same as the substrate free energy. In this case, the wetting layer is compressively strained in a few percent. Interestingly note that in the original publication by Stranski and Krastanov, no strain effects were considered. The strain relaxation leads to the formation of coherent (dislocation free) islands on top of a thin wetting layer. Depending on the strain value and its sign, the growth of QDs, the formation of nanopits or even QDs–nanopits cooperative structure can be achieved.

Binary III-V compound semiconductors, especially nitrides and their ternary and quaternary alloys are very attractive for several applications [6]. For instance, GaInN alloys are used for fabrication of blue and green light emitted diodes, as well as for violet and blue lasers [7]. Since the band gap of GaInN can be varied from 2.0 to 3.5 eV by increasing of GaN concentration, the potential operating wavelengths cover nearly the entire visible spectra range [8, 9]. High-speed field effect transistors, high-temperature electronic devices, UV and blue light emitters, detectors and gas sensors were made of GaN [10]. Among III-nitride semiconductors, InN has the lowest effective mass and small band gap. Therefore, InN-related solid solutions can extend the emission or absorption from the UV to near infrared regions. The photovoltaic (PV) and thermo-PV cells were also fabricated using InN [10].

While zinc-blend film/zinc-blend substrate combinations have been analyzed previously [11], systems involving hexagonally oriented material as either the film or substrate have not been thoroughly investigated. Examples of important semiconductor materials that exist in the hexagonal crystal structure include the wide bandgap compound

semiconductors GaN, SiC and many II–VI semiconductors. The growth of hexagonal materials has been extensively studied experimentally, however, quantitative calculation of the inherent strain energy has not been fully performed. Furthermore, the effect of the strain energy on the resulting equilibrium has not been addressed. In [12], elastic compliance equations are developed and their relationship to the overall strain energy of a hexagonally oriented film and substrate are presented. These general relations are then applied to the growth of GaN on different substrates. Additionally, the sufficient lattice mismatch between the III-N binary compounds allows growing of nanostructures 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 [13] that nanoscale indium composition fluctuation due to InGaIn 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 [14]. 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 [13, 14] without using any antisurfactants. High-density GaN/AlN QDs for deep UV LED with high quantum efficiency [15] have been also successfully grown by molecular beam epitaxy.

In this paper, the competing growth mechanism of QDs or nanopits in GaN-InN-AlN material system both for zinc-blend and wurtzite configurations is theoretically investigated using the continuum elasticity model proposed by J. Tersoff (IBM) [1, 16]. Additionally, miscibility gap analysis for the GaInAlN quaternary material system is performed by the Gibbs free energy calculations.

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2. Calculation of the Islands Total Energy in GaInAlN Material System

At the calculation of the total energy, we assume that islands and pits have a shape as schematically presented in Fig. 1(a). High-resolution SEM images of the InAsSbP composition pyramidal island and a nanopit [4] grown on InAs(100) substrate are presented in Fig. 1(b).

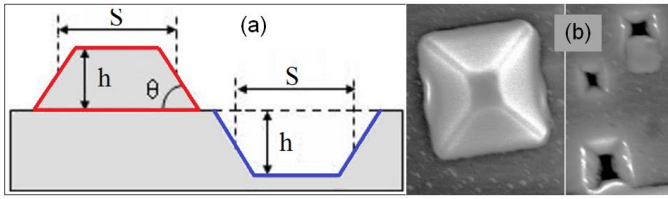


Fig. 1 Schematic view of the island-nanopit structure's cross section - (a), high-resolution SEM images of the InAsSbP composition pyramidal island and a nanopit - (b, c) [4]

As it is known [16], the energy for the formation of an island (or a pit) can be written as $E = E_S + E_R$, where E_S and E_R are the changes in surface energy and the reduction of the strain energy by elastic relaxation, respectively. Considering island's volume as a constant, in the case of $s = t = h \cot \theta$, where s , t , h and θ are the length, width, height (depth) and contact angle, as in figure 1(a), the energy is equal to [1, 16]:

$$E = 4\Gamma V^{2/3} T \tan^{1/3} \theta - 6cVT \tan \theta, \quad (1)$$

where $\Gamma = \gamma_e C_{sc} \theta - \gamma_s C_{ot} \theta$. For the crystals with a cubic symmetry, $\gamma_s = \frac{1}{2} \epsilon^2 (C_{11} + C_{44}) d_{wet}$, $c = \sigma_b^2 \frac{(1-\nu)}{2\pi\mu}$, $\sigma_b = \epsilon (C_{11} + C_{44})$. Here γ_s and γ_e are the surface energy per unit area for the normal orientation and the beveled edge, respectively, $\epsilon = \frac{\Delta a}{a}$ 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 $\gamma_{sl} = \gamma_s - \gamma_e \cos \theta$ [17], where for Stranski-Krastanov growth mode $\gamma_{sl} = 0$, $\nu = \frac{\lambda}{2(\lambda + \mu)}$ is the Poisson ratio, λ , μ and C_{ij} are the Lamé coefficients and the elastic modulus of the substrate. Finally, the expressions for the total energy for the crystals with a zinc-blend and a wurtzite symmetry, respectively, can be written as:

$$E = 4(\gamma_e C_{sc} \theta - \frac{1}{2} \epsilon^2 (C_{11} + C_{44}) d_{wet}(\epsilon) \cot \theta) V^{2/3} T \tan^{1/3} \theta - 3\epsilon^2 (C_{11} + C_{44})^2 \cdot \frac{(1-\nu)}{\pi\mu} \cdot VT \tan \theta \quad (2)$$

$$E = 4(\gamma_e C_{sc} \theta - \frac{1}{511+512} \epsilon^2 d_{wet}(\epsilon) \cot \theta) V^{2/3} T \tan^{1/3} \theta - 3\epsilon^2 \left(\frac{S_{11}-S_{12}}{S_{11}^2-S_{12}^2} \right)^2 \cdot \frac{(1-\nu)}{\pi\mu} \cdot VT \tan \theta, \quad (3)$$

$$\text{where } S_{11} = \frac{(C_{11} \cdot C_{33} - C_{13}^2)}{(C_{11} - C_{12})(C_{11} \cdot C_{33} + C_{12} \cdot C_{33} - 2C_{13}^2)}, \quad S_{12} = \frac{(C_{13}^2 - C_{12} \cdot C_{33})}{(C_{11} - C_{12})(C_{11} \cdot C_{33} + C_{12} \cdot C_{33} - 2C_{13}^2)}$$

[12]. Next, we performed a mathematical approximation of experimental data [18] in order to evaluate for the GaInAlN material system an analytical expression for the dependence of wetting layer thickness versus strain. In our calculations we used the following expressions for d_{wet} in monolayers (ML): (i) if the deformation strain is positive, then $d_{wet} = 0.05\epsilon^{-3/2}$ at $\epsilon > 0.03$ [18] and $d_{wet} = 24.184e^{-31.034\epsilon}$ at $0 < \epsilon < 0.03$ (accuracy of approximation $R^2 = 0.9635$), (ii) if the deformation strain is negative, then $d_{wet} = 0.15|\epsilon|^{-3/2}$ at $|\epsilon| > 0.035$ [18], and $d_{wet} = 45.162e^{-23.034|\epsilon|}$ at $0 < |\epsilon| < 0.035$ (accuracy of approximation $R^2 = 0.9934$).

The results of theoretical calculations of the dependence of GaInAlN composition islands energy on volume at different strains for zinc-blend and wurtzite symmetry, calculated at $\gamma_e = 10.15 \times 10^{-5} \text{ J/cm}^2$, $\mu = 30.3 \times 10^4 \text{ J/cm}^3$, $C_{11} = 272.3 \times 10^3 \text{ J/cm}^3$, $C_{44} = 130.3 \times 10^3 \text{ J/cm}^3$, $\nu = 0.361$ and $\theta = 0.785 (45^\circ)$ and $\gamma_e = 2 \times 10^{-5} \text{ J/cm}^2$, $\mu = 106 \times 10^4 \text{ J/cm}^3$, $C_{11} = 296 \times 10^3 \text{ J/cm}^3$, $C_{12} = 130.3 \times 10^3 \text{ J/cm}^3$, $C_{13} = 158 \times 10^3 \text{ J/cm}^3$, $C_{33} = 267 \times 10^3 \text{ J/cm}^3$, $C_{44} = 241 \times 10^3 \text{ J/cm}^3$, $\nu = 0.37$ $\theta = 0.785 (45^\circ)$ are presented in Fig. 2(a). The dependence of islands critical volume versus strain for the zinc-blend and wurtzite structures are presented in Figs. 2(b and c), respectively.

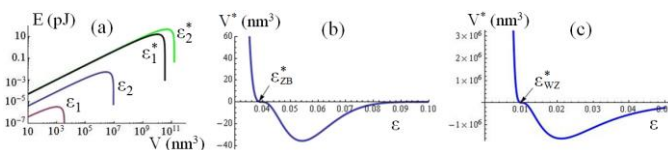


Fig. 2 Dependence of the GaInAlN strain-induced zinc-blend and wurtzite islands energy versus volume at different strains ($\epsilon_1[\text{ZB}] = \epsilon_1^*[\text{WZ}] = 0.01$ and $\epsilon_2 = \epsilon_2^* = 0.008$) - (a). Critical volume at zinc-blend - (b) and wurtzite - (c) structures versus strain

As it can be seen from Fig. 2(a), in order to attain a stable geometry the island must first overcome the energy barrier E^* which occurs at volume V^* . It is also quite visible that both E^* and V^* strongly depend on the strain and dramatically decrease at the increasing of the strain. At the critical strain of $\epsilon^* = 0.039$ for zinc-blend and $\epsilon^* = 0.01$ for wurtzite symmetry, the sign of critical volume (Figs. 2(b and c)) is changed. We assume that at $\epsilon = \epsilon^*$ the mechanism of the nucleation is changed from the growth of dots to the nucleation of pits. Clearly, at small misfit ($\epsilon < \epsilon^*$), the bulk nucleation mechanism dominates. However, at $\epsilon > \epsilon^*$, 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. From Fig. 2(a) also visible, that at the same strain the critical volume for the formation of a stable island for the wurtzite structure is at least three orders higher than that for the zinc-blend structure. Additionally, Figs. 2(b and c) show that the critical strain for the wurtzite structure almost four times smaller than that for a zinc-blend structure.

3. Miscibility Analysis for Zinc-Blend and Wurtzite GaN-InN-AlN Material System

Next, in order to analyze the miscibility task for the zinc-blend and wurtzite GaN-InN-AlN material system, we calculated the Gibbs free energy of mixing using the following relationship:

$$\Delta G(x, y) = \Delta H - T\Delta S, \quad (4)$$

where T is the absolute temperature, ΔH and ΔS are the enthalpy and entropy of mixing, respectively, which are determined by the following expressions [6]:

$$\Delta H(x, y) = \alpha_{\text{GaN-InN}}(1-x-y)x + \alpha_{\text{InN-AlN}}xy + \alpha_{\text{GaN-AlN}}(1-x-y)y \quad (5)$$

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

Here α is the parameter of pseudobinary interaction, and R the universal gas constant. The interaction parameter α is the characteristic index of immiscibility tension. According to the model of "delta-lattice parameter" (DLP) [19, 20], the interaction parameter is represented in the form,

$$\alpha_{AB} = 4k \left[\frac{1}{2} (a_A^{-2.5} + a_B^{-2.5}) - \left(\frac{a_A + a_B}{2} \right)^{-2.5} \right], \quad (6)$$

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 $1.15 \times 10^7 \text{ cal/(mole} \times \text{\AA)}$ [19-21]. 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 zinc-blend and wurtzite AlGaIn, InGaIn and AlInN ternary systems at different temperatures are shown in Fig. 3. Eq.(4) was used for calculations, certainly, taking into account Eqs. (5) and (6).

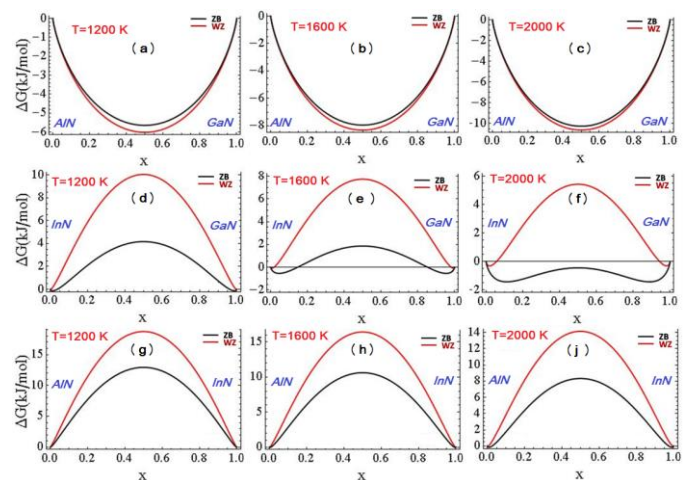


Fig. 3 One mole Gibbs free energy versus concentration for zinc-blend and wurtzite AlN-GaN - (a-c), InN-GaN - (d-f) and AlN-InN - (g-j) alloys, respectively at T=1200 K, 1600 K and 2000 K

It is seen from Fig. 3 that as distinct from AlN-GaN alloys, 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 will decay into two separate solid phases [21]. From Fig. 3 also visible that the immiscibility gap for the wurtzite structure is larger than that for zinc-blend structure at the same technological conditions.

Schematic 3D patterns of molar Gibbs free energy of mixing depending on composition of the zinc-blend and wurtzite GaInAlN material system at $T=1200$ K, $T=1600$ K and $T=2000$ K temperatures are presented in Fig. 4. In Fig. 5, the iso-energetic cut-offs of GaInAlN material system's Gibbs free energy for zinc-blend (Figs. 5(a-c)) and wurtzite (Figs. 5(d-f)) structures at different energies and in the temperature range of $T=600$ - 2000 K, are presented.

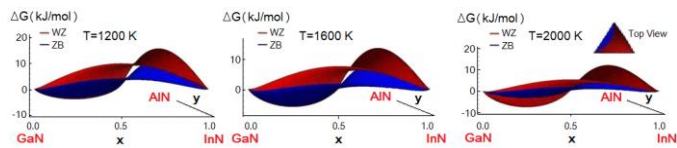


Fig. 4. 3D schematic patterns of one mole Gibbs free energy of the GaInAlN material system for zinc-blend and wurtzite structures at $T=1200$ K, 1600 K and 2000 K

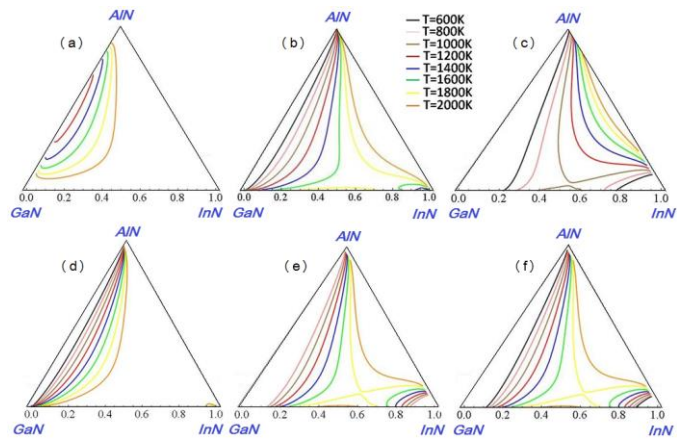


Fig. 5. Iso-energetic cut-offs of GaInAlN material system's Gibbs free energy for zinc-blend - (a-c) and wurtzite - (d-f) structures at different temperatures. (a, d) - $\Delta G = -5$ kJ/mol, (b, e) - $\Delta G = 0$ kJ/mol, (c, f) - $\Delta G = +5$ kJ/mol

Actually, our calculations and Figs. 4 and 5 show that there is no immiscibility gap in AlN-GaN material system. In spite of that system, for the InN-GaN, an incorporation of components is energetically favorable only up to around 1mol%, after that the immiscibility occurs both for zinc-blend and wurtzite structure. For the AlN-InN material system the situation is more dramatically. Here, mutual incorporation of components is energetically favorable only up to impurity levels. However, evidently the immiscibility gaps for both InN-GaN and AlN-InN solid solutions decrease at temperature increasing.

4. Conclusion

Thus, the growth mechanism of QDs and nanopits in GaN-InN-AlN material system for both zinc-blend and wurtzite structures is theoretically investigated using continuum elasticity model. The islands energy versus their volume, as well as the critical energy and volume versus the island and wetting layer lattice constants relative mismatch ratio (ϵ) are calculated. It was shown that when the zinc-blend GaN is used

as a substrate and when the strain between the wetting layer and a substrate overcomes critical $\epsilon^* = 0.039$ value, instead of QDs nucleation, the formation of nanopits becomes energetically preferable. Otherwise, when wurtzite GaN is used as a substrate the critical strain is equal to $\epsilon^* = 0.01$, i.e. up to four times smaller. The results also show that at the same strain the critical volume for the formation of a stable island for the wurtzite structure is at least three orders higher than that for the zinc-blend structure. The miscibility analysis for GaInAlN quaternary material system has shown that immiscibility gap strongly depends not only on temperature, but also on crystallographic structure. In particular, for the wurtzite structure an immiscibility gap is larger than that for the zinc-blend structure at the same technological conditions. Presented results can be useful at QDs engineering, as well as at the growth of multicomponent bulk crystals and epitaxial thin films in GaInAlN material system.

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