# Competing nucleation of islands and nanopits in zinc-blend III-nitride quaternary material system

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**Abstract**. The growth mechanism of quantum dots (QDs), nanopits and collaborative QDs-nanopits structures in GaN-InN-AlN material system is theoretically investigated using the 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 (strain $\varepsilon$), are calculated. It is 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 $\varepsilon^* = 0.039$ value, instead of QDs nucleation, the formation of nanopits becomes energetically preferable. Revealed feature is critical and has to be taking into account at QDs engineering in GaInAlN material system.

## 1. Introduction

During the last two decades, the use of quantum dots (QDs), corresponding semiconducting materials and their band gap engineering, opens up entirely new functionalities of traditional devices as well as new challenges for the fabrication of devices with unique properties. In particularly, single photon sources for quantum cryptography, quantum dot 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–Krastanow 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 Krastanow, 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 alloy are very attractive for several applications [5]. For instance, GaInN alloys are used for fabrication of blue and green light emitted diodes, as well as for violet and blue lasers [6]. 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 [7,8]. High-speed field effect transistors, high-temperature electronic devices, UV and blue light emitters, detectors and gas sensors were made of GaN [9]. Among III-nitride semiconductors, InN has 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 [9].

Additionally, the sufficient lattice mismatch between the III-N binary compounds allows growing of nanostructures in Stranski–Krastanow growth mode.

In this paper, the growth mechanism of QDs, nanopits and collaborative QDs-nanopits structures in GaN-InN-AlN material system is theoretically investigated using the continuum elasticity model proposed by J. Tersoff (IBM) [1,10].

## 2. Total energy of island–pit structure in GaN-InN-AlN material system

Here, according to [10] we assume that the zinc-blend GaN substrate has only discrete orientations and therefore only one angle can be used [10]. We also assume that islands and pits have a shape as schematically presented in figure 1(*a*). High-resolution SEM images of the InAsSbP composition pyramidal island and a nanopit [4] grown on InAs(100) substrate are presented in Figures 1(*b*,*c*).

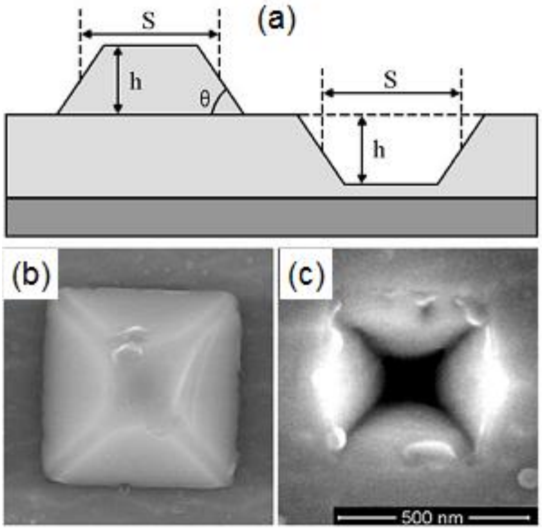


**Figure 1.** Schematic view of the island-nanopit structure's cross section – (*a*), high-resolution SEM images of the InAsSbP composition pyramidal island and a nanopit – (*b*, *c*).

As it is known from [10], the total Gibbs free 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 change in surface energy 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 $\theta$ are the length, width, height (depth) and contact angle, as in figure 1(*a*), the energy is equal to:

$$E = 4\Gamma V^{2/3} \mathrm{Tan}^{1/3}\theta - 6 c V \mathrm{Tan}\theta \tag{1}$$

where $\Gamma = \gamma_e \mathrm{Csc}\theta - \gamma_s \mathrm{Cot}\theta$. 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 $\gamma_s$ and $\gamma_e$ 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 $\gamma_e$ can be found from Young equation $\gamma_{sl} = \gamma_s - \gamma_e \mathrm{Cos}\theta$ [11], where for Stranski–Krastanow 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, $\mu$, $\lambda$ and $C_{ij}$ are the Lame coefficients and the elastic modulus of the substrate. Finally, the expression for the total energy can be written as:

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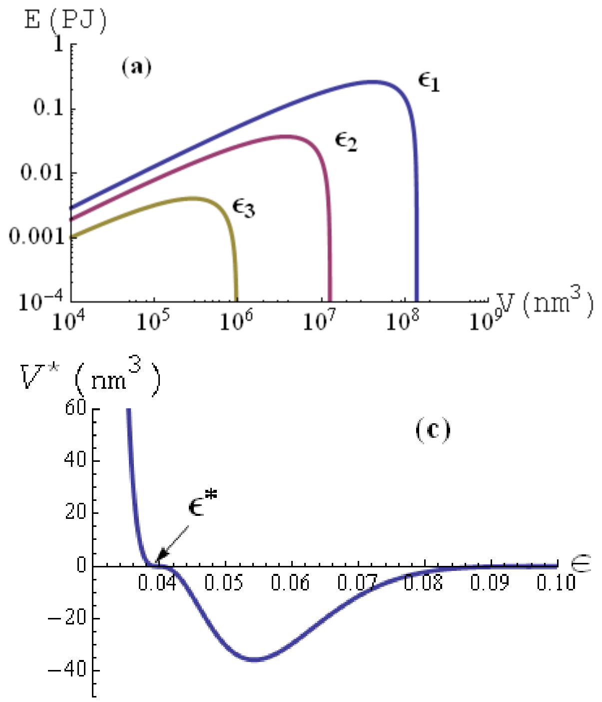
$$E = 4\left(\gamma_e Csc\theta - \frac{1}{2}\varepsilon^2 (C_{11} + C_{44}) d_{wet}(\varepsilon) Cot\theta\right) V^{2/3} Tan^{1/3}\theta - \\ -3\varepsilon^2 (C_{11} + C_{44})^2 \cdot \frac{(1-\nu)}{\pi\mu} \cdot V\, Tan\theta \quad (2)$$

Next, we performed a mathematical approximation of experimental data [12] 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 $d_{wet} = 0.05\varepsilon^{-3/2}$ at $\varepsilon > 0.03$ [12] and $d_{wet} = 24.181 e^{-31.034\varepsilon}$ 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 $|\varepsilon| > 0.035$ [12] and $d_{wet} = 45.162 e^{-23.03|\varepsilon|}$ at $0 < |\varepsilon| < 0.035$ (accuracy of approximation $R^2 = 0.9934$).

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



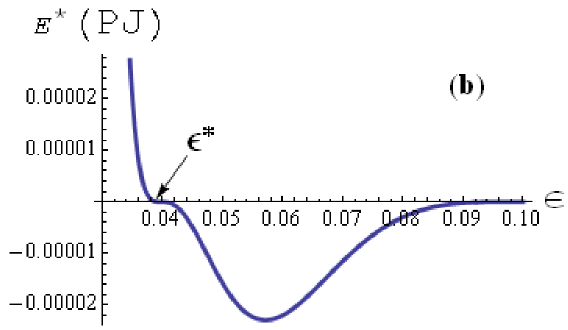




**Figure 2** (color online). (*a*) – dependence of the GaInAlN composition islands energy on volume at different strain ($\varepsilon_1$=0.02, $\varepsilon_2$=0.025, $\varepsilon_3$=0.03). (*b,c*) – critical energy and critical volume versus strain, respectively.

From Figure 2(*a*) it is quite visible that an island has to overcome the energy barrier $E^*$ which reached at volume $V^*$. Figures 2(*b*) and 2(*c*) show the dependences of the critical energy and critical volume versus strain, respectively. Our calculations show the evident result, i.e. both $E^*$ and $V^*$ depend on the strain and that at some critical strain of $\varepsilon^* = 0.039$ the sign of energy and volume is changed. According to the islands configuration (figure 1(*a*)), as well as question (2), we conclude that $\varepsilon^*$ is the edge of the strain for island nucleation, after that the formation of a pit becomes energetically preferable.

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## 3. Conclusion

Thus, the growth mechanism of QDs, nanopits and collaborative QDs-nanopits structures in GaN-InN-AlN material system was investigated using the theoretical approach proposed by J. Tersoff (IBM). The islands energy versus their volume, as well as the critical energy and volume versus the strain, are calculated. When the zinc-blend GaN is used as a substrate, it was shown that when the strain between the wetting layer and a substrate overcomes critical $\varepsilon^*=0.039$ value, the formation of nanopits becomes energetically preferable instead of QDs nucleation. Revealed feature has to be taking into account not only at QDs engineering but also at the growth of bulk crystals and epitaxial thin films in GaInAlN material system.

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