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Towards Ideal Quantum Dots

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Abstract. Arrays of single photon emitters with the same energy of luminescence are necessary for the development of quantum imformation technology. The studied epitaxial quantum dots have an undresired inhomogeneity of luminescence. Here, $A_xB_{1-x}C_yD_{1-y}$ alloys of *AC*, *AD*, *BC* and *BD* compounds are presented as semiconductors in which non-random distribution of cations and anions may result in self-assembling of identical tetrahedral clusters. It can be due to the preference of *AC* and *BD* bonding over *AD* and *BC* one, a decrease of the strain energy or both of them. The self-assembling conditions of 1P4Ga clusters in AlN-rich $Al_xGa_{1-x}P_yN_{1-y}$ alloys with Ga and phosphorus contents in the dilute and ultra dilute limits, correspondingly, are represented. All phosphorus atoms should be in 1P4Ga clusters at ~1000 °C if the Ga content reaches several percents. AlN-rich $Al_xGa_{1-x}P_yN_{1-y}$ alloys with 1P4Ga clusters are promising semiconductors for fabrication of arrays of identical single photon emitters with the same energy of luminescence.

Keywords: Quaternary submolecular semiconductor alloys; self-assembling; identical clusters.

Introduction. Arrays of identical single photon emitters are necessary for quantum information technology and quantum cryptography [1]. One of the important requisites for ideal single photon emitters is the same energy of luminescence. Epitaxial semiconductor quantum dots have been extensively studied because of their possible application as robust solid-state single photon sources [2]. Epitaxial semiconductor quantum dots with the linear sizes, normally, not smaller than 5 nm are obtained as a result of transformation of the highly lattice mismatch epitaxial layer on the semiconductor substrate [3]. The dispersion in sizes in all three directions is usually significant and it leads to an undesirable inhomogeneity in the emission energy. Therefore, the problem of the formation of identical in shape, size and composition zero-dimensional semiconductor objects or ideal quantum dots remains very important.

Self-assembling of 1As4Ga and 1N4Al tetrahedral clusters in $Ga_xAl_{1-x}As_yN_{1-y}$ and in $Al_xGa_{1-x}N_yAs_{1-y}$ semiconductor alloys, correspondingly, was predicted in [4]. Such self-assembling leads to the formation of an ensemble of identical in shape, size and composition ~1 nm zero-dimensional semiconductor objects in semiconductor matrix. Later self-assembling of tetrahedral identical clusters was described for a number of $A_x^{III}B_{1-x}^{III}C_y^{V}D_{1-y}^{V}$ and $A_x^{II}B_{1-x}^{II}C_y^{VI}D_{1-y}^{VI}$ semiconductor alloys [5]. All such clusters are zero-dimensional objects embedded in a semiconductor matrix. Their luminescent properties should be close to those of ~1 nm nanocrystals. It is known that ~1 nm CdS nanocrystals form excitons [6]. It demonstrates that excitons form in ~1 nm semiconductor objects. Therefore, the formation of excitons in self-assembled ~1 nm clusters embedded in wide band gap semiconductor matrix is highly probable. The self-assembled identical clusters may be considered as ideal quantum dots because of the same size, shape and composition. AlN has the widest band gap among III-V semiconductors. Therefore, the study of self-assembling of tetrahedral clusters in AlN-rich alloys is very promising from the single photon emitters fabricating standpoint. Among AlN-rich alloys the self-assembling conditions for AlN-rich $Ga_xAl_{1-x}P_yN_{1-y}$ alloys are not studied yet. Here the statistical thermodynamics of $A_xB_{1-x}C_yD_{1-y}$ semiconductor alloys and self-assembling conditions of 1P4Ga tetrahedral clusters in AlN-rich $Ga_xAl_{1-x}P_yN_{1-y}$ alloys are presented.

$A_xB_{1-x}C_yD_{1-y}$ submolecular alloys

$A_xB_{1-x}C_yD_{1-y}$ quaternary semiconductor alloys include $A_x^{III}B_{1-x}^{III}C_y^{V}D_{1-y}^{V}, A_x^{II}B_{1-x}^{II}C_y^{VI}D_{1-y}^{VI}$ and $A_x^{IV}B_{1-x}^{IV}C_y^{VI}D_{1-y}^{VI}$ alloys. Their crystal lattice consists of two mixed sublattices filled with two types of atoms. Any atom in $A_xB_{1-x}C_yD_{1-y}$ can have the different nearest neighbour atoms as it is seen in Fig. 1. a. $A_xB_{1-x}C_yD_{1-y}$ are alloys of four binary compounds *AC*, *AD*, *BC* and *BD* since there are four types of chemical bonds corresponding to these compounds. $A_xB_{1-x}C_yD_{1-y}$ alloys are submolecular alloys since their crystal structure is a mixture of chemical bonds. They differ from well known supramolecular alloys such as, for example, $A_xB_yC_{1-x-y}D$ (alloys) (Fig. 1. b.) in which there (are) **is** one mixed sublattice [7]. The crystal structure of $A_xB_yC_{1-x-y}D$ consists of three sets of groups of one-type chemical bonds *AD*, *BD* and *BC* situated around *A*, *B* and *C* atoms. Such groups are considered as molecules. Therefore, they are supramolecular alloys.

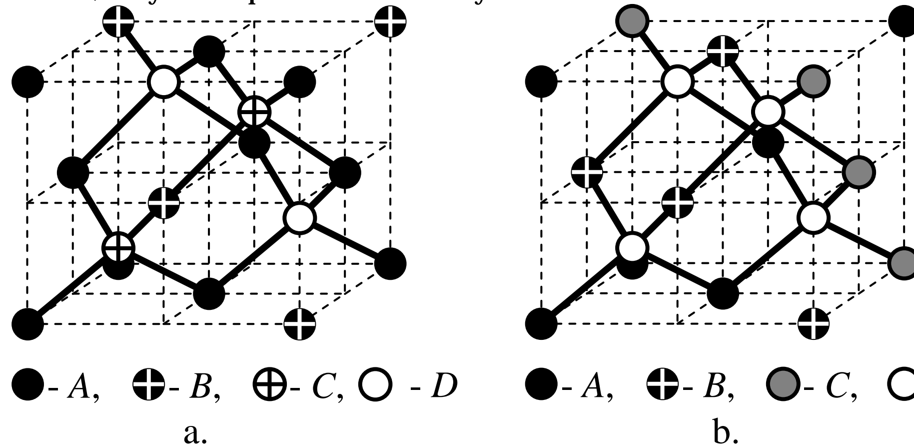

Figure 1. a. $A_xB_{1-x}C_yD_{1-y}$ submolecular alloy with the zinc blende structure; b. $A_xB_yC_{1-x-y}D$ supramolecular alloy with the zinc blende structure.

According to the electroneutrality condition, the number of cations in $A_xB_{1-x}C_yD_{1-y}$ alloy is equal to the number of anions: $N_A + N_B = N_C + N_D = N$. The numbers of four kinds of chemical bonds *AC*, *AD*, *BC* and *BD* are connected by three relations given as

$$N_{AC} + N_{AD} = z_1 N_A,\ N_{AC} + N_{BC} = z_1 N_C,\ N_{AC} + N_{AD} + N_{BC} + N_{BD} = z_1 N,$$

where z_1 is the coordination number of the nearest neighbour atoms [8]. Four kinds of chemical bonds and three relations between them lead to the absence of a one to one correspondence between the numbers of atoms (concentrations of atoms or elemental compositions *x* and *y*) and numbers of chemical bonds (concentrations of bonds or chemical compositions x_{AC}, x_{AD}, x_{BC} and x_{BD}). One elemental composition corresponds to a vast set of the chemical compositions. Indeed, the exchange of the lattice sites between different cations or anions can lead to the reaction between chemical bonds that is given as

$$nAC + nBD = nAD + nBC, n = 1,..., z_1. \quad (1)$$

where $z_1 = 4$ for alloys with the zinc blende and wurtzite structures and $z_1 = 6$ for alloys with the sodium chloride structure. Number *n* in the reaction depends on the nearest surroundings of cations or anions participating in the exchange. Reaction $nAC + nBD = nAD + nBC$ varies the numbers of chemical bonds and, thus, one elemental composition corresponds to a very large quantity of the chemical compositions. This circumstance distinguishes $A_xB_{1-x}C_yD_{1-y}$ submolecular alloys from $A_xB_yC_{1-x-y}D$ supramolecular alloys. The concentrations of bonds in $A_xB_yC_{1-x-y}D$ alloys (Fig. 1. b) are equal to $x_{AD} = x$, $x_{BD} = y$ and $x_{BC} = 1 - x - y$. Thus, there is a one to one correspondence between the elemental and chemical compositions in $A_xB_yC_{1-x-y}D$ alloys.

First, the concentrations of bonds in $A_xB_{1-x}C_yD_{1-y}$ alloys were estimated on the basis of the assumption that cations and anions are distributed at random [8]. A number of properties and characteristics of $A_x^{III}B_{1-x}^{III}C_y^{V}D_{1-y}^{V}$ and $A_x^{II}B_{1-x}^{II}C_y^{VI}D_{1-y}^{VI}$ semiconductor alloys were described on the

basis of this assumption. However, the thermodynamic characteristics of the constituent compounds and internal strains should lead to the non-random distribution of cations and anions. For the first time, the non-random distributions were considered in [9]. The distributions of cations and anions in $A_{x}^{III}B_{1-x}^{III}C_{y}^{V}D_{1-y}^{V}$ described in [9] are **s**lightly different from random. It is due to the fact that the thermodynamic characteristics and lattice parameters of the constituent compounds of the considered alloys are not very different. A non-random distribution results in an increase of atomic clusters different in shape, size and composition. The arrangement of atoms on the lattice sites corresponds to the minimum condition of the free energy. The Gibbs and Helmholtz free energies of solids are almost equal. Therefore, the Helmholtz free energy is normally used for the description of $A_xB_{1-x}C_yD_{1-y}$ alloys. The molar Helmholtz free energy of $A_xB_{1-x}C_yD_{1-y}$ alloys is given as

$$f = f^{CC} + u^{SE} - Ts^{C}, \tag{2}$$

where $f^{CC} = \sum_{i,j=1}^{2} f_{ij}x_{ij}, (i = A, B; j = C, D)$ is the sum of the free energies of the constituent compounds, f_{ij} and x_{ij} are the molar free energies and concentrations of the *ij*-th compound, u^{SE} is the molar strain energy, T and s^C are the absolute temperature and molar configurational entropy, correspondingly. The swap of the lattice sites results in the variation of all three summands in (2). Therefore, three causes lead to the non-random distribution of atoms in $A_xB_{1-x}C_yD_{1-y}$ alloys. The reaction (1) is the first of them. The transformation of pairs of the chemical bonds changes the sum of the free energies of the constituents since the sums of the free energies of *AC*, *BD* and *AD*, *BC* compounds are not equal. Accordingly, the bonding of the pair of compounds having the smaller value of the sum of the free energies is preferential. The second reason is the internal strains caused by the difference in the lattice parameters of the constituent compounds. The strain energy is derived using the valence force field model [10, 11]. In this model, the strained state is described by using two types of elastic constants. The constants of the first type called the bond stretching constants are the elastic constants of bonds. The constants of the second type named the bond bending elastic constants are the elastic constants of angles between bonds. The elastic constants of semiconductors with the zinc blende structure are obtained from the system of equations written as

$$3\alpha - 18.5C_{11}R - 11.5C_{12}R - 29\beta = 0,$$

$$0.433(\alpha+\beta) - 2.57\left[(C_{11}+C_{12})R + 1.73\beta\right]$$

$$-\frac{\left[0.433(\alpha-\beta) - 5.55(C_{11}R - C_{12}R - 1.73\beta)\right]^2}{0.433(\alpha+\beta) - 5.02(C_{11}R - C_{12}R - 1.73\beta)} - C_{44}R = 0,$$

where α and β are also the bond stretching and bond bending elastic constants, correspondingly, R is the bond length of the undistorted crystal and C_{ij} are the stiffness coefficients. These elastic constants of the same semiconductor with the zinc blende and wurtzite structures differ insignificantly [11]. The deformation energy of the primitive cell of semiconductor with the zinc blende structure is given as

$$u = \frac{1}{2}\alpha\left(\frac{3}{4R^2}\right)\sum_{i=1}^{4}\left[\Delta\left(r_i^1 \cdot r_i^1\right)\right]^2 + \frac{1}{2}\sum_{s=1}^{2}\beta^s\left(\frac{3}{4R^2}\right)\sum_{i,j>i}\left[\Delta\left(r_i^s \cdot r_j^s\right)\right]^2$$

where $\Delta\left(r_i^1 \cdot r_i^1\right) = R_i^2 - r_{ij}^2$ and $\Delta\left(r_i^1 \cdot r_i^2\right) = \left(R_i^2 - r_i^2\right)\cos\varphi$ are the scalar variations, where r_i^s and r_j^s are bond vectors about atom *s*, φ is the angle between the bonds [10]. Accordingly, the deformation energies of bonds and angles are given, correspondingly, as

$$u = \frac{3\alpha}{8R^2}(R^2 - r^2)^2 \text{ and } u = \frac{3\beta}{8R^2}(R^2\cos\varphi_0 - r^2\cos\varphi)^2$$

where R and r, φ_0 and φ are the distances between the nearest atoms and the angles between bonds in the undistorted and distorted crystals, respectively. The data on the bond stretching and bond bending elastic constants for a number of semiconductors are available [10-12] or can be calculated. The entropy of $A_xB_{1-x}C_yD_{1-y}$ non-random alloy is smaller than that of the same random

one. Therefore, the non-random distribution can occur due to a decrease of the sum of the free energies of the constituents or decrease of the strain energy or both of them.

The significant preferential formation of AlN bonds was experimentally established in GaAs-rich $Al_xGa_{1-x}N_yAs_{1-y}$ alloys ($y < 0.02$, $x >> y$) with the zinc blende structure [13]. GaN bonds were almost absent in these alloys. The authors explained the dominance of chemical bonding by the large cohesive energy of AlN bonds. However, the bonding in $Al_xGa_{1-x}N_yAs_{1-y}$ has more complex nature. $Al_xGa_{1-x}N_yAs_{1-y}$ belong to $A_xB_{1-x}C_yD_{1-y}$ alloys. The exchange of the lattice sites between cations or anions in $Al_xGa_{1-x}N_yAs_{1-y}$ leads to the transformation of bonds that corresponds to the reaction between bonds nAlN + nGaAs → nAlAs + nGaN ($1 \le n \le 4$) or vice versa. Accordingly, the AlN bonding in $Al_xGa_{1-x}N_yAs_{1-y}$ should be accompanied by the formation of GaAs bonds. The preferential AlN and GaAs bonding is caused by the smaller value of the sum of the AlN and GaAs free energies in comparison with the sum of the AlAs and GaN free energies.

The most interesting result of the preferential AlN and GaAs bonding is self-assembling of identical tetrahedral clustes (1N4Al and 1As4Ga clusters) with nitrogen and As central atoms in GaAs- and AlN-rich $Al_xGa_{1-x}N_yAs_{1-y}$ ($x >> y$ or $1 - x >> 1 - y$), correspondingly. The prediction of this phenomenon and the equation conditions of the free energies of the random alloys and alloys in which all nitrogen or As atoms are in clusters were done in [4]. The phase diagram of $Al_xGa_{1-x}N_yAs_{1-y}$ with the self-assemblilng conditions of 1N4Al and 1As4Ga clusters in GaAs-and AlN-rich alloys, respectively, was described in [14]. Later, the similar diagrams were obtained for ZnTe-rich $Mg_xZn_{1-x}O_yTe_{1-y}$, AlN-rich $Al_xGa_{1-x}Sb_yN_{1-y}$; ZnTe-rich $Sr_xZn_{1-x}O_yTe_{1-y}$; GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$, ZnTe-rich $Ca_xZn_{1-x}O_yTe_{1-y}$, ZnS-rich $Ca_xZn_{1-x}O_yS_{1-y}$ alloys [5]. An occurrence of clusters variated in shape, size and composition is hardly probable in these alloys since it should lead to an increase of the free energy. Accordingly, the described self-assembling is a way to form an array of identical zero-dimensional objects embedded in the semiconductor matrix.

Self-assembling of 1P4Ga clusters in $Ga_xAl_{1-x}P_yN_{1-y}$ alloys

The self-assembling conditions of 1P4Ga clusters in AlN-rich $Ga_xAl_{1-x}P_yN_{1-y}$ are represented in this Chapter. The Helmholtz free energy of such alloys is a sum of the free enhergies of the constituent compounds, strain energy and configurational entropy term $f = f^{CC} + u^{SE} - Ts^C$. GaP, GaN, AlP and AlN are the constituent compounds. The clustering degree is represented by the cluster order parameter α that is a portion of phosphorus atoms situated in 1P4Ga clusters. This parameter can vary from zero to unity. The alloys with $\alpha = 0$, $0 < \alpha < 1$ and $\alpha = 1$ are disordered, partially cluster ordered and completely cluster ordered alloys, correspondingly [14]. The dilute and ultra dilute limits for the Ga and phosphorus contents, respectively, are considered. Phosphorus atoms should be distributed randomly because of their very small concentration. The sum of the free energies of the constituent compounds is given as

$$\begin{aligned} f &= xyf_{\mathrm{GaP}} + x(1-y)f_{\mathrm{GaN}} + (1-x)yf_{\mathrm{AlP}} + (1-x)(1-y)f_{\mathrm{AlN}} + \\ &+ \alpha(1-x)y\left(f_{\mathrm{GaP}} - f_{\mathrm{GaN}} - f_{\mathrm{AlP}} + f_{\mathrm{AlN}}\right) \end{aligned}. \quad (3)$$

The variation of the sum (3) as a result of self-assembling depends only on the relation between the free energies $\Delta f = f_{\mathrm{GaP}} - f_{\mathrm{GaN}} - f_{\mathrm{AlP}} + f_{\mathrm{AlN}}$. Therefore, only last item of the sum (3) is taken into account. The relation between the free energies is expressed as

$$\Delta f = \Delta h^f - T\Delta s ,$$

where $\Delta h^f = h^f_{\mathrm{GaP}B} - h^f_{\mathrm{GaN}} - h^f_{\mathrm{Al}B} + h^f_{\mathrm{AlN}}$, $\Delta s = s_{\mathrm{GaP}} - s_{\mathrm{GaN}} - s_{\mathrm{AlP}} + s_{\mathrm{AlN}}$, h^f_{GaP} and s_{GaP} are the molar enthalpy of formation and molar entropy of GaP. Accordingly, the relation may be rewritten as

$$\Delta f = \Delta h^{f0} - T\Delta s^0 + \int_{298.15}^{T} \Delta c_P dT - T\int_{298.15}^{T} \frac{\Delta c_P}{T} dT ,$$

where $\Delta h^{f0} = h^{f0}_{\mathrm{GaP}} - h^{f0}_{\mathrm{GaN}} - h^{f0}_{\mathrm{AlP}} + h^{f0}_{\mathrm{AlN}}$, $\Delta s^0 = s^0_{\mathrm{GaP}} - s^0_{\mathrm{GaN}} - s^0_{\mathrm{AlP}} + s^0_{\mathrm{AlN}}$, $\Delta c_P = c_P^{\mathrm{GaP}} - c_P^{\mathrm{GaN}} - c_P^{\mathrm{AlP}} + s_P^{\mathrm{AlN}}$, h^{f0}_{GaP}, s^0_{GaP} are the molar enthalpy of formation and entropy of GaP at STP, correspondingly, and c_P^{GaP} is the heat capacity of GaP. GaP and AlP crystallize with the zinc blende structure. GaN and AlN in the stable state crystallize with the wurtzite structure and with

the zinc blende structure in the metastable state. The distinction between the enthalpies of the same compound of the different crystal modifications depends mainly on the coordination number, distance between atoms and Madelung constant [15]. The distances between atoms in the zinc blende and wurtzite modifications of a compound as well as the Madelung constants are almost equal [13]. Thus, the difference between the enthalpies of a compound with the zinc blende and wurtzite structures should be insignificant. The enthalpies of formation and entropies at STP and heat capacities were taken from [16]. The value of relation $\Delta f = f_{\mathrm{GaP}} - f_{\mathrm{GaN}} - f_{\mathrm{AlP}} + f_{\mathrm{AlN}}$ demonstrates significant preference of the GaP and AlN bonding.

The strain energy of AlN-rich $Ga_xAl_{1-x}P_yN_{1-y}$ alloys is given as

$$u = xu_{\mathrm{Ga}} + yu_{\mathrm{P}} + \alpha y\left(u_{\mathrm{1P4Ga}} - u_{\mathrm{P}} - 4u_{\mathrm{Ga}}\right) \quad \textbf{(4)}$$

where $u_{1P4Ga} = 1.683\times10^5$ J/mole, $u_P = 1.354\times10^5$ J/mole and $u_{Ga} = 2.572\times10^3$ J/mole are the strain energies caused by 1P4Ga clusters and isolated phosphorus and Ga atoms, respectively. The strain energies caused by clusters as well as isolated atoms were estimated as sums of two items. The first item is the strain energy of quadruples of tetrahedral cells situated around the central atoms of clusters or around isolated Ga and phosphorus atoms. A quadruple of 1Ga1P3N tetrahedral cells situated around the central atom of 1P4Ga cluster is shown in Fig. 2.

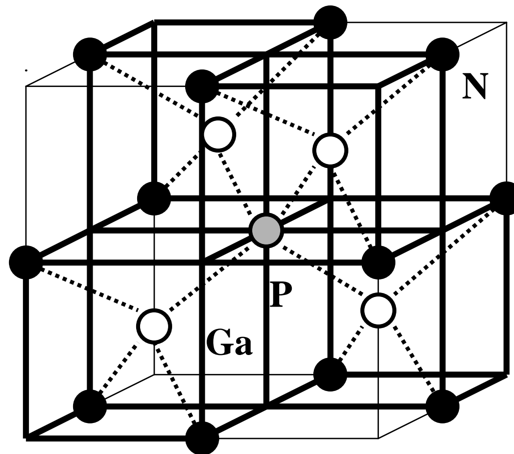

Figure 2. 1P4Ga cluster in $Ga_xAl_{1-x}P_yN_{1-y}$ alloy with the zinc blende structure. (A quadruple of 1Ga1P3N tetrahedral cells situated around the central atom of 1P4Ga cluster).

This part is described within the framework of the valence force field model by the approach developed for the estimation of the strain energy of III-V ternary alloys [17]. The averages of the bond bending elastic constants of the compounds are used as elastic constants of the angles between the unlike bonds. The deformation energies of the crystal lattice outside the quadruples are the second items. These energies are obtained as the deformation energies of the elastic media with radial displacements inversely proportional to the square of a distance from the central atoms of the quadruples. The considerable differences between the lattice parameters of nitrides and phosphides result in significant strains around 1P4Ga clusters and isolated phosphorus atoms. The closeness of the covalent radii of Al and Ga leads to the insignificant strains caused by isolated Ga atoms. It is very important for fabrication of identical single photon emitters since 1P4Ga clusters should be in the same internal strains.

The entropy term is written as

$$-Ts = -RT\ln\Omega_1\Omega_2 = RT\left[\left(x-4\alpha y\right)\ln\frac{x-4\alpha y}{1-4\alpha y} + \left(1-x\right)\ln\frac{1-x}{1-4\alpha y} + y\ln y + (1-y)\ln(1-y)\right],$$

where $\Omega_1\Omega_2$ is the number of configurations. The first factor is the number of the permutations of Ga and Al atoms outside 1P4Ga clusters at the fixed arrangement of isolated phosphorus atoms and clusters. The second factor is a number of anion arrangements. The mean values of the distances between isolated phosphorus atoms and 1P4Ga clusters are much larger then the distances between the nearest neighbor atoms. In such a case, spatial correlations among

isolated phosphorus atoms as well as among 1P4Ga clusters are very small since the phosphorus content is in the ultra dilute limit. In fact, 1P4Ga clusters and isolated phosphorus atoms should be distributed randomly.

The cluster order parameter is obtained under the minimum condition of the Helmholtz free energy that is written as $\frac{\mathrm{d}f}{\mathrm{d}\alpha}=0$. Clusters should occur when the minimum condition for the Helmholtz free energy given as $\frac{\mathrm{d}f(\alpha=0)}{\mathrm{d}\alpha}=0$ is fulfilled. The condition of the self-assembling completion when all phosphorus atoms are in clusters is the minimum condition of the Helmholtz free energy written as $\frac{\mathrm{d}f(\alpha=1)}{\mathrm{d}\alpha}=0$.

The self-assembling conditions for $Ga_xAl_{1-x}P_yN_{1-y}$ alloys were considered in the following content ranges $4y \le x \le 0.06$ and $1\times10^{-8} \le y \le 1\times10^{-4}$. 1P4Ga clusters are the identical zero-dimensional objects with the size ~1 nm embedded in AlN-rich matrix. The composition of such objects in accordance with the numbers and types of the chemical bonds corresponds to $GaP_{0.25}N_{0.75}$ alloy. The band gaps of GaP and GaN are significantly smaller than that of AlN. The exciton energies of zero-dimensional objects increase with a decrease of their sizes and like this the exciton energies of CdS nanocrystals increase up to 3.5 eV, when the nanocrystal diameter reaches 1 nm [6]. It exceeds 1 eV the band gap of bulk CdS. But even with such excess, the energy of excitons formed in ~1 nm $GaP_{0.25}N_{0.75}$ objects should be significantly smaller then the value of the band gap of AlN-rich matrix. Therefore, the formation of excitons by self-assembled 1P4Ga clusters is highly probable. Furthermore, clusters are in the insignificant strain field caused by highly mismatched clusters and by isolated phosphorus atoms located on the considerable separations from each other. Accordingly, 1P4Ga clusters and isolated phosphorus atoms cannot change the band gap due to very small concentrations of the highly lattice mismatched phosphorus atoms. In fact, they are isolated objects capable to form the localized states in AlN-rich semiconductor matrix.

The fulfilled estimates demonstrate that the self-assembling occurrence temperatures do not depend on the phosphorus content. It is due to the chosen phosphorus content. But the temperatures of the self-assembling completion depend on the Ga and phosphorus contents. The difference between the temperatures of the self-assembling occurrence and completion of self-assembling decreases with the decrease of the phosphorus content. The cluster occurrence and self-assembling completion temperatures of $Ga_xAl_{1-x}P_yN_{1-y}$ alloy with $x = 4y$ and $y = 1\times10^{-4}$ are equal, respectively, to 266.2 °C and 0 °C. The self-assembling occurrence temperature and difference in the temperatues of the self-assembling occurrence and completion as functions of the Ga content are shown in Figs. 3 and 4 for $Ga_xAl_{1-x}P_yN_{1-y}$ alloys with $y = 1\times10^{-4}$.

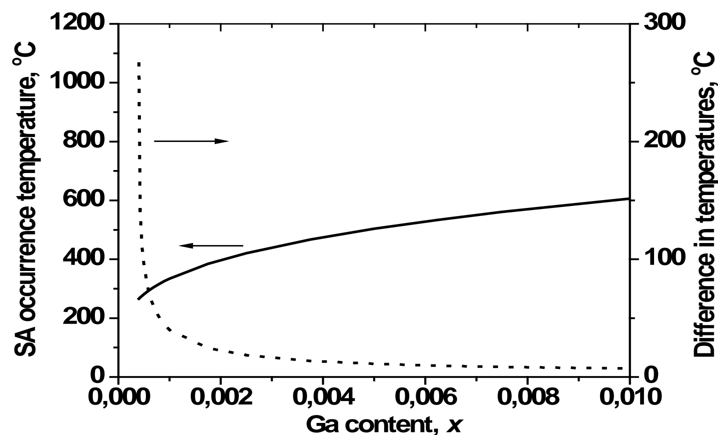

Figure 3. The self-assembling occurrence temperature (solid curve) and difference in the temperatues of the self-assembling occurrence and completion (dotted curve) on Ga content at phosphorus content $y = 1\times10^{-4}$.

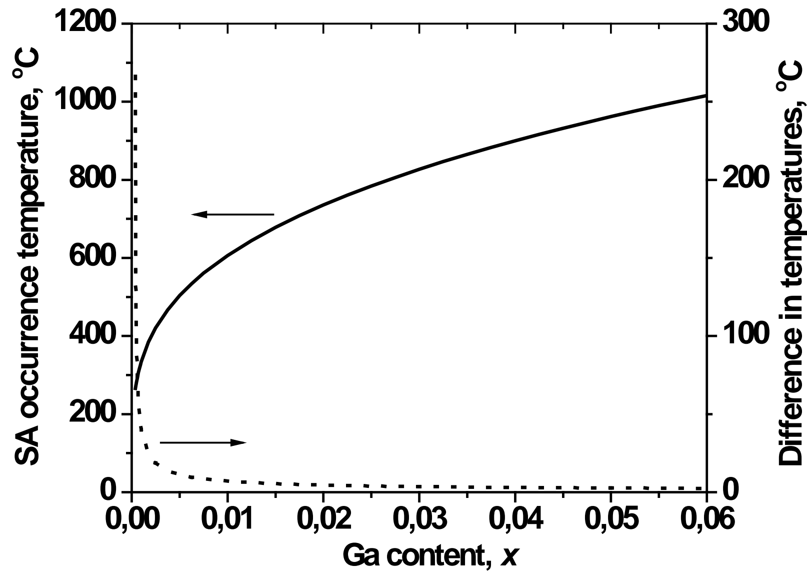

Figure 4. The self-assembling occurrence temperature (solid curve) and difference in the temperatues of the self-assembling occurrence and completion (dotted curve) on Ga content at phosphorus content $y = 1\times10^{-4}$.

As it is seen from Fig. 4 these temperatures increase up to more than 1000 °C at $x = 0.06$. The metalorganic chemical vapor deposition and molecular beam epitaxy are the most suitable technologies for the growth of $Ga_xAl_{1-x}P_yN_{1-y}$ alloys. Normally, the growth processes of the metalorganic chemical vapor deposition and molecular beam epitaxy are strongly non-equilibrium. Therefore, the formation of non-equilibrium disordered $Ga_xAl_{1-x}P_yN_{1-y}$ (alloys) are highly probable. The redistribution of Ga atoms leading to self-assembling may be reached by the thermal annealing of a disordered alloy. The thermal annealing of GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ epitaxial films at ~700 °C is an efficient method of redistribution of atoms [18]. $Ga_xAl_{1-x}P_yN_{1-y}$ alloys belong to the same type just as $In_xGa_{1-x}N_yAs_{1-y}$ alloys. Therefore, the annealing should also be the efficient method in order to redistribute Ga atoms in $Ga_xAl_{1-x}P_yN_{1-y}$ alloys. The completely cluster ordered $Ga_xAl_{1-x}P_yN_{1-y}$ form at (the) high temperatures if the Ga content reaches several percents (Fig. 4). Thus, the high temperature annealing may be used to redistribute Ga atoms if disordered $Ga_xAl_{1-x}P_yN_{1-y}$ alloy formed.

The temperature dependencies of the enthalpy and heat capacity of $Ga_xAl_{1-x}P_yN_{1-y}$ are shown in Fig. 5 (a, b).

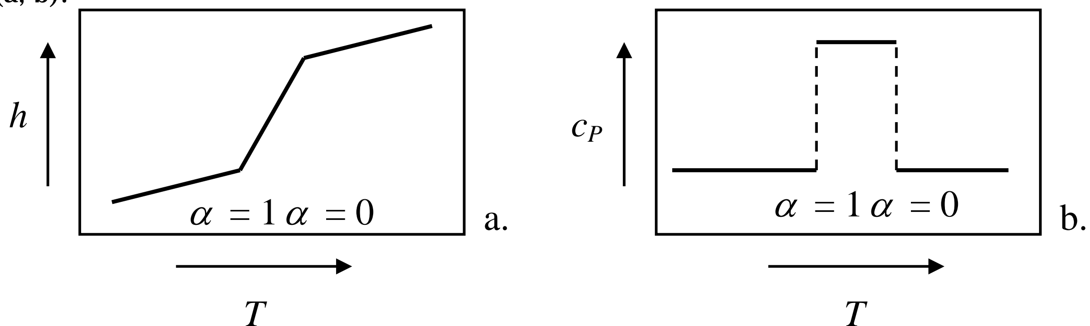

Figure 5. The temperature dependencies of the enthalpy (a) and heat capacity (b)

The enthalpy is a continuous function of temperature. The heat capacity has two finite discontinuities. Thus, the alloys undergo two second-order phase transitions at the cluster occurrence and self-assembling completion in accordance with the Ehrenfest's classification scheme of the phase transitions [19]. The fulfilled estimates demonstrate that AlN-rich Ga_xAl_{1-}

${}_xP_yN_{1-y}$ alloys should be the very promising wide band gap semiconductors with an array of identical ~1 nm low band gap zero-dimensional objects.

Conclusions: $A_xB_{1-x}C_yD_{1-y}$ semiconductor alloys widely used in optoelectronics are promising materials for fabrication of arrays of single photon emitters with the same energy of luminescence. It is due to self-assembling of clusters identical in shape, size and composition. The self-assembling conditions of 1P4Ga clusters in AlN-rich $Al_xGa_{1-x}P_yN_{1-y}$ alloys are represented. Such clusters are ~1 nm zero-dimensional objects with composition equivalent to $GaP_{0.25}N_{0.75}$ alloy. Thus, such clusters are identical low band gap objects embedded in the wide band gap AlN-rich matrix. Accordingly, excitons captured by these clusters should have the same energy of luminescence.

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На пути к идеальным квантовым точкам

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Аннотация. В статье методами статистической термодинамики показано, что в четверных полупроводниковых сплавах $A_xB_{1-x}C_yD_{1-y}$ должны самоорганизовыватася идентичные кластеры. Такие кластеры должны быть идеальными квантовыми точками. Условия самоорганизции 1P4Ga кластеров в $Ga_xAl_{1-x}P_yN_{1-y}$ сплавах получены в большом диапазоне температур и составов.

Ключевые слова: Четверные полупроводниковые сплавы; Самоорганизация; Идентичные кластеры.