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New view on $In_xGa_{1-x}N_yAs_{1-y}$ alloys

Vyacheslav A. Elyukhin*

Departamento de Ingenieria Electrica, Centro de Investigacion y de Estudios Avanzados del Instituto Politecnico Nacional, Avenida Instituto Politecnico Nacional 2508, 07360, Mexico, Mexico

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* e-mail elyukhin@cinvestav.mx, Phone: +52 55 5747 3773, Fax: +52 55 5061 3978

Semiconductors with isoelectronic centers are actively studied to fabricate arrays of identical single photon emitters. Self-assembling of 4N10In and 1N4In clusters in GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ is represented. All or almost all In atoms are in 4N10In clusters from 0 to 800 °C in $In_xGa_{1-x}N_yAs_{1-y}$ with $x = 1\times10^{-4}$, $y = 1\times10^{-4}$ and $x = 1\times10^{-5}$, $y = 1\times10^{-5}$. All or almost all nitrogen atoms are in 1N4In clusters if $x = 0.01$, $y = 1\times10^{-4}$ and $x = 1\times10^{-3}$, $y = 1\times10^{-6}$. There are both types of clusters in alloys with $x = 5\times10^{-5}$, $y = 5\times10^{-7}$; $x = 2\times10^{-4}$, $y = 2\times10^{-6}$; $x = 1\times10^{-4}$, $y = 1\times10^{-5}$ and $x = 2\times10^{-3}$, $y = 2\times10^{-4}$ and portions of nitrogen atoms in clusters depend on the composition and temperature. Thus, $In_xGa_{1-x}N_yAs_{1-y}$ are promising semiconductors to obtain arrays of identical isoelectronic clusters with the desirable density.

1 Introduction $In_xGa_{1-x}N_yAs_{1-y}$ alloys lattice matched to GaAs with nitrogen in the dilute limit are actively studied now [1, 2]. Such alloys with nitrogen in the ultra dilute limit also may be very interesting from a device application standpoint. Semiconductors with isoelectronic centers are promising materials to fabricate arrays of the identical single photon emitters required for quantum computers [3]. Quantum computers should considerably improve computational power [4]. Among III-V semiconductors, GaAs:N is one of the most studied since the nitrogen dyads bound excitons [3, 5]. However, nitrogen is the highly mismatched isoelectronic impurity in GaAs. Therefore, nitrogen dyads produce significant strains in GaAs:N. Moreover, the significant density of dyads leads to the considerable decrease of the configurational entropy. Such GaAs:N can be formed only under non-equilibrium growth conditions and should be in the thermodynamically unstable state with respect to the transformation of dyads in isolated nitrogen atoms. It is a serious disadvantage of GaAs:N. Normally, it is desirable to use thermodynamically stable or metastable semiconductors to fabricate devices.

GaAs:(B, Sb) with self-assembled isoelectronic impurity clusters was proposed to resolve this problem [6]. Self-assembling (SA) of 4B10Sb and 1B4Sb clusters is preferable in GaAs:(B, Sb) in the wide impurity composition and temperature ranges. 4B10Sb clusters are empty tetrahedrons surrounded by Sb atoms and in 1B4Sb clusters boron atoms are in the centers of Sb tetrahedrons. SA of such clusters compensates considerably the tension and compression caused, respectively, by isolated boron and Sb atoms and, thus, reduces the internal strains. This reduction is one of the causes of SA. Moreover, GaAs:(B, Sb) is GaAs-rich $B_xGa_{1-x}Sb_yAs_{1-y}$ alloy of BSb, BAs, GaSb and GaAs. In such alloy an exchange of lattice sites between cations or anions may lead to the reaction between bonds: nB-Sb + nGa-As → nB-As + nGa-Sb, (n = 1,..,4) or vice versa. BSb and GaAs bonding is thermodynamically preferential over the BAs and GaSb one. SA of the clusters increases B-Sb and Ga-As bond concentrations and, correspondingly, decreases B-As and Ga-Sb bond concentrations. The transformation of B-Sb and Ga-As bonds into B-As and Ga-Sb bonds is the second reason of SA.

The similar situation is in $In_xGa_{1-x}N_yAs_{1-y}$ alloys. They are alloys of InN, InAs, GaN and GaAs. InN and GaAs bonding is also thermodynamically preferential over InAs and GaN one. Moreover, SA of 4N10In and 1N4In clusters should compensate the internal strains produced by In and nitrogen isolated atoms. However, SA in GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ is not studied yet. Moreover, epitaxial technologies of such alloys are well developed now. It is an additional advantage of GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ as materials to fabricate electronic devices. SA conditions in $In_xGa_{1-x}N_yAs_{1-y}$ are considered here.

2 Model The free energy of GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ alloy is considered as a sum of the free energies of constituent compounds InN, InAs, GaN and GaAs, strain energy and entropy term $g = g^0 + u - Ts$. 4N10In and 1N4In clustering degrees are represented by 4N10In cluster order parameter α (4N10In COP) and 1N4In cluster order parameter β (1N4In COP), respectively. The parameters are ratios between the total number of nitrogen atoms and numbers of nitrogen atoms in 4N10In and 1N4In clusters, correspondingly. 4N10In and 1N4In clusters are shown in Figs. 1 and 2.

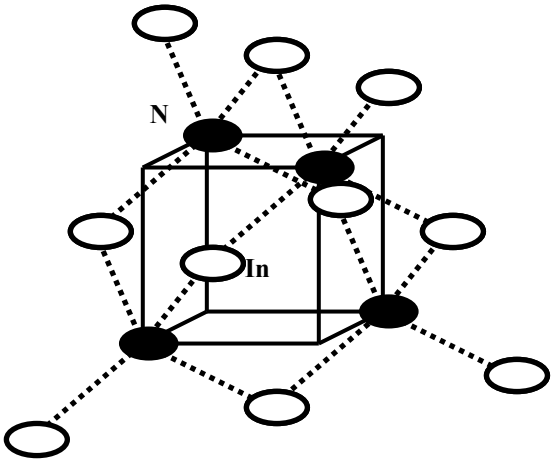

Figure 1 4N10In cluster.

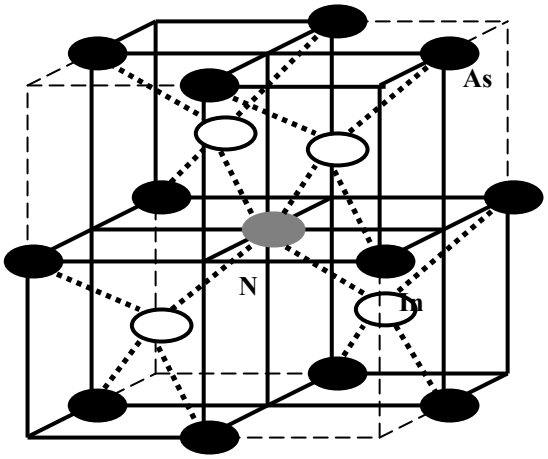

Figure 2 1N4In cluster in GaAs-rich matrix

The sum of the free energies of constituent compounds is written as

$$g^0 = \Delta\mu(\alpha+\beta)(1-x)y + \Delta\mu xy + \mu_{GaAs} + (\mu_{InAs} - \mu_{GaAs})x + (\mu_{GaN} - \mu_{GaAS})y, \quad (1)$$

where $\Delta\mu = \mu_{InN} - \mu_{InAs} - \mu_{GaN} + \mu_{GaAs}$ and μ_{InN} is the chemical potential of InN. The change of the sum (1) under variations of 4N10In and 1N4In COPs depends only on the first item. Therefore, only it will be taken into account further. The relation $\Delta\mu$ between the free energies is

$$\Delta\mu = \Delta h - T\Delta s,$$

where $\Delta h = h_{InN} - h_{InAs} - h_{GaN} + h_{GaAs}$, $\Delta s = s_{InN} - s_{InAs} - s_{GaN} + s_{GaAs}$, h_{InN} and s_{InN} are the enthalpy and entropy of InN, respectively. The value of the relation $\Delta h = h_{InN} - h_{InAs} - h_{GaN} + h_{GaAs}$ is equal to the value of the relation $\Delta h^f = h^f_{InN} - h^f_{InAs} - h^f_{GaN} + h^f_{GaAs}$, where h^f_{InN} is the enthalpy of formation of InN. The relation Δh^f is given by

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

where $\Delta h^{f0} = h^{f0}_{InN} - h^{f0}_{InAs} - h^{f0}_{GaN} + h^{f0}_{GaAs}$, h^{f0}_{InN} is the standard enthalpy of formation of InN, $\Delta c_P = c_P^{InN} - c_P^{InAs} - c_P^{GaN} + c_P^{GaAs}$ and c_P^{InN} is the heat capacity of InN. The relation Δs was estimated as

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

where $\Delta s^0 = s^0_{InN} - s^0_{InAs} - s^0_{GaN} + s^0_{GaAs}$ and s^0_{InN} is the standard entropy of InN. The standard enthalpies of formation and standard entropies as well as the heat capacities of the constituent compounds are available [7]. The estimated values of the relation between the free energies of the constituent compounds $\Delta\mu$ demonstrate a significant preferential InN and GaAs bonding over a InAs and GaN one. The strain energy of $In_xGa_{1-x}N_yAs_{1-y}$ is given by

$$u = (1-\alpha-\beta)yu_N + (x - 2.5\alpha y - 4\beta y)u_{In} + 0.25\alpha y u_{4N10In} + \beta y u_{1N4In},$$

where u_{In}, u_N, u_{4N10In} and u_{1N4In} are the strain energies due to isolated In and nitrogen atoms and clusters, correspondingly. The strain energies caused by both isolated atoms and 1N4In clusters were estimated as sums of two items. The first item is the strain energy of quadruples of tetrahedral cells situated around isolated In and nitrogen atoms or central atoms of 1N4In clusters. This part was described by using the valence force field model and the approach developed to estimate the strain energy of III-V ternary alloys [8]. The elastic constants of bonds and angles between bonds of the constituent compounds are available [9, 10]. The other contribution is the deformation energy outside of the quadruples. This part was considered as the energy of the elastic media with radial displacements inversely proportional to the square of a distance from the central atoms of quadruples. The strain energies due to isolated In and nitrogen atoms and 1N4In clusters are equal, respectively, to $u_{In} = 1.099\times10^4$ Jmol^{-1}, $u_N = 1.323\times10^5$ Jmol^{-1} [11] and $u_{1N4In} = 3.314\times10^4$ Jmol^{-1}. The strain energy due to 4N10In clusters equal to $u_{4N10In} = 8.368\times10^4$ Jmol^{-1} was obtained as the deformation energy of clusters in the unstrained GaAs-rich matrix to reduce the number of unknown variables in

the calculations. Therefore, this strained energy should be overestimated. However, even the overestimated value demonstrates a considerable decrease of the strain energy after SA of 4N10In clusters. The strain energy due to 4N10In clusters was estimated also in the framework of the valence force field model as a sum of the deformation energies of bonds and angles between bonds [8]. Elastic constants of bonds are much larger than those of angles between bonds. Therefore, deformations of angles between bonds should be preferential in 4N10In clusters. The strain energies due to isolated In and nitrogen atoms and clusters were obtained by their minimizing. The strain energies demonstrate the tendency to SA of clusters of both types. However, SA of 4N10In clusters decreases the strain energy much more than SA of 1N4In clusters since angles between bonds are mainly distorted in larger clusters.

The entropy term is written as

$$-Ts = RT(1-\alpha)y\ln\frac{(1-\alpha)y}{1-\alpha y} + RT(1-y)\ln\frac{1-y}{1-\alpha y}$$
$$+RT\left(x-\frac{10}{4}\alpha y-4\beta y\right)\ln\frac{x-\frac{10}{4}\alpha y-4\beta y}{1-\frac{10}{4}\alpha y-4\beta y}$$
$$+RT(1-x)\ln\frac{1-x}{1-\frac{10}{4}\alpha y-4\beta y}$$
$$+RT(1-\alpha-\beta)y\ln\frac{1-\alpha-\beta}{1-\alpha}+RT\beta y\ln\frac{\beta}{1-\alpha}$$
$$+\frac{1}{10}RT\alpha y\ln\frac{27\alpha y}{20}+\frac{2}{27}RT\ln\frac{20-27\alpha y}{20}.$$

The entropy is the function of a number of different configurations. This number was obtained as a product of two factors. The first factor is a number of permutations of atoms when isolated In and nitrogen atoms as well as and 1N4In clusters are distributed randomly at a fixed location of 4N10In clusters. The second factor is a number of arrangements of 4N10In clusters. 4N10In and 1N4In COPs were obtained by minimizing the free energy.

3 Results and discussion The compositions of $In_xGa_{1-x}N_yAs_{1-y}$ were considered from $x = 1\times10^{-5}$ to $x = 0.01$ and from $y = 1\times10^{-7}$ to $y = 2\times10^{-4}$ since, in such a case, both type of clusters should be isolated objects and can bound the excitons. The temperature range from 0 °C to 800 °C was chosen for the estimates. In spite of the fact that 800 °C is a too high temperature for epitaxial growth of GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$, it was chosen since a thermal annealing may be necessary to obtain the equilibrium state of an alloy with clusters. The considerable structural changes in $In_{0.06}Ga_{0.94}N_{0.002}As_{0.998}$ with the increase of In-N bonds after 30 min annealing at 700 °C were observed [12]. The higher nitrogen $In_{0.06}Ga_{0.94}N_{0.02}As_{0.98}$ layers have also been annealed for ≈ 100 min at 600, 650 and 700 °C. After annealing the concentrations of In-N bonds in these samples are also increased as well as in $In_{0.06}Ga_{0.94}N_{0.002}As_{0.998}$ [12]. Apparently, $In_xGa_{1-x}N_yAs_{1-y}$ layers grown by the metalorganic chemical vapor deposition were formed under the non-equilibrium conditions since a thermal treatment results in the increase of In-N bonds decreasing the strain energy.

SA of clusters of any type reduces a sum of the free energies of constituent compounds, the strain energy and the entropy. The transformation of 4N10In cluster into two 1N4In clusters and isolated In and nitrogen atoms increases a sum of the free energies of constituent compounds, the strain energy and the entropy. The transformation (4N10In) + 2(In) → 3(1N4In) + 1(N) increases the sum of the free energies, decreases the strain energy and increases the entropy. The transformation (4N10In) + 6(In) → 4(1N4In) decreases the strain energy and changes the entropy. The variation of the entropy as a result of this transformation depends on In and nitrogen contents. Thus, SA of 4N10In and 1N4In clusters are competing processes.

All or almost all nitrogen atoms should be in 1N4In clusters over the entire temperature range in $In_xGa_{1-x}N_yAs_{1-y}$ with concentrations $x = 0.01$, $y = 1\times10^{-4}$ and $x = 0.001$, $y = 1\times10^{-5}$ due to a smaller decrease of the entropy after SA. The temperature dependencies of COPs for $In_xGa_{1-x}N_yAs_{1-y}$ with concentrations $x = 5\times10^{-5}$, $y = 5\times10^{-7}$; $x = 1\times10^{-4}$, $y = 1\times10^{-6}$ and $x = 2\times10^{-4}$, $y = 2\times10^{-6}$ are shown in Fig. 3.

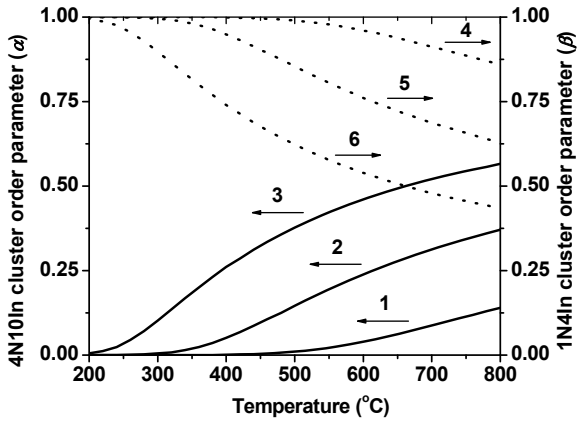

Figure 3 The temperature dependencies of 4N10In COPs (solid curves) and 1N4In COPs (dotted curves) for $In_xGa_{1-x}N_yAs_{1-y}$ with $x = 5\times10^{-5}$, $y = 5\times10^{-7}$ (curves 1 and 4), $x = 1\times10^{-4}$, $y = 1\times10^{-6}$ (curves 2 and 5) and $x = 2\times10^{-4}$, $y = 2\times10^{-6}$ (curves 3 and 6).

Almost all nitrogen atoms are in both types of clusters at 800 °C and the portion of nitrogen atoms in clusters increases up to 100 % with a decrease of temperature. The curves in Fig. 3 demonstrate the significant transformation of 1N4In clusters into 4N10In with an increase of temperature. The temperature dependencies of COPs for $In_xGa_{1-x}N_yAs_{1-y}$ with $x = 1\times10^{-4}$, $y = 1\times10^{-5}$; $x = 1\times10^{-3}$, $y = 1\times10^{-4}$ and $x = 2\times10^{-3}$, $y = 2\times10^{-4}$ are shown in Fig. 4. Larger nitrogen contents lead to preferential SA of 4N10In

clusters at higher temperatures. All or almost all In atoms should be in 4N10In clusters over the entire temperature range in the alloys with concentrations $x = y = 1\times10^{-4}$ and x

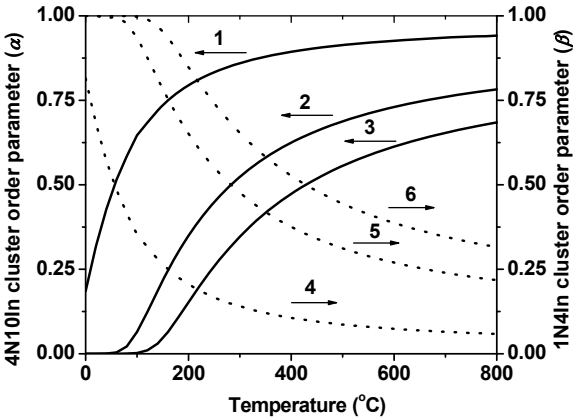

Figure 4 The temperature dependencies of 4N10In COPs (solid curves) and 1N4In COPs (dotted curves) for $In_xGa_{1-x}N_yAs_{1-y}$ with $x = 1\times10^{-4}$, $y = 1\times10^{-5}$ (curves 1 and 4), $x = 1\times10^{-3}$, $y = 1\times10^{-4}$ (curves 2 and 5) and $x = 2\times10^{-3}$, $y = 2\times10^{-4}$ (curves 3 and 6).

$= y = 1\times10^{-5}$. It demonstrates that $In_xGa_{1-x}N_yAs_{1-y}$ may be obtained with a desired density of clusters as well as required densities of both of them.

Ga-N bonds formed by isolated nitrogen atoms and In-N bonds in 1N4In clusters are expanded, respectively, on 4.54% and 1.34% in $In_xGa_{1-x}N_yAs_{1-y}$. It is one of the causes why SA of 1N4In clusters decreases the strain energy more than five times. Ga-N bonds formed by isolated nitrogen atoms in GaP:N are expanded on 4.12% and in spite of this tension isolated nitrogen atoms form bound excitons with the small binding energy (8×10^{-3} eV). This small binding energy is due to considerable lattice strains around nitrogen atoms [13]. The binding energies in unstrained semiconductors due to the different electronegativities of isoelectronic impurities and host atoms should be of the order of 1 eV [13]. The difference between the electronegativities of nitrogen and As is larger than that of nitrogen and phosphorus. Therefore, the formation of excitons bound to 1N4In clusters in $In_xGa_{1-x}N_yAs_{1-y}$ is highly probable. In-N bonds in 4N10In clusters are extended on 2.61% (12 bonds) and 3.08% (4 bonds). Thus, nitrogen atoms in 4N10In clusters are exposed to less strains than isolated nitrogen atoms in GaAs:N and GaP:N. Accordingly, the formation of exciton traps by 4N10In clusters is also highly probable.

$In_xGa_{1-x}N_yAs_{1-y}$ epitaxial layers onto GaAs with the small In and nitrogen contents $x = 0.023$, $y = 2.4\times10^{-4}$ [14] were successfully grown. Apparently, in accordance with the results on structural changes during the annealing of $In_xGa_{1-x}N_yAs_{1-y}$ [12], a thermal treatment is necessary to transform $In_xGa_{1-x}N_yAs_{1-y}$ in alloys with the self-assembled clusters since In and nitrogen contents are small. Only 1N4In clusters with 1N4In COP $\beta \approx 1$ should form in $In_xGa_{1-x}N_yAs_{1-y}$ with $x = 0.023$, $y = 2.4\times10^{-4}$ at 800 °C. Fast cooling of annealed alloys should form "frozen" states of a crystal structure with clusters. The estimates demonstrate that there are the conditions under which it is possible to form GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ having 4N10In and 1N4In clusters. High temperature treatment of such alloys is, apparently, necessary to form the clusters. The formation of bound excitons in GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ with 1N4In and 4N10In clusters is highly probable due to small strains around nitrogen atoms.

4 Conclusion GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ alloys with self-assembled 4N10In and 1N4In clusters are profitable in the wide temperature and concentration ranges. The type of clusters and their densities depend on temperature and composition. The clusters are in the insignificant strain field and the formation of excitons bounded to the clusters is highly probable. Thus, $In_xGa_{1-x}N_yAs_{1-y}$ are promising candidates to fabricate arrays of single photon emitters

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