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Self-assembling of impurity clusters in AlN:(Ga, B^V, C^V), (B^V, C^V = P, As; P, Sb; As, Sb)

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ABSTRACT

The self-assembling conditions of arrays of tetrahedral impurity clusters of two types in zinc blende AlN:(Ga, B^V, C^V), (B^V, C^V = P, As; P, Sb; As, Sb) are represented. Doping with one cation and two anion isoelectronic impurities transforms AlN into AlN-rich $Ga_xAl_{1-x}B^V{}_yC^V{}_zN_{1-y-z}$ alloy of GaB^V, GaC^V, GaN, AlB^V, AlC^V and AlN. The cause of self-assembling is the preference of GaB^V, GaC^V and AlN bonding over that of GaN, AlB^V, AlC^V. The conditions are considered from 0 °C to 1000 °C in the dilute and ultra dilute limits for the cation and anion impurities, correspondingly. The temperature ranges between the cluster occurrence and self-assembling completion when the same anion impurities are in clusters are very small. 1P4Ga and 1As4Ga cluster occurrence temperatures are equal, correspondingly, to 797 °C and 736 °C at Ga content 2% and P and As contents 0.01%. 1P4Ga and 1Sb4Ga cluster occurrence temperatures are equal, correspondingly, to 976 °C and 736 °C at the same impurity contents. The cluster densities in AlN:(Ga, As, Sb) are close to those in AlN:(Ga, P, Sb). The results demonstrate that studied semiconductors are promising materials to produce arrays of identical ~1 nm low band gap objects of two types embedded in the wide band gap matrix.

1. Introduction

Arrays of identical single photon emitters are expected to play an important role in quantum information technology to fabricate quantum computers which would improve computational power [1]. Epitaxial quantum dots (EQDs) or zero-dimensional low band gap objects embedded in a wide band gap host semiconductor matrix are widely studied now as candidates for single photon emitters [2,3]. However, size, shape and composition distributions leading to undesirable inhomogeneity of the emission energy hinder the application of EQDs. Therefore, a search of ways to form identical zero-dimensional low band gap objects embedded in a wide band gap semiconductor matrix is an important problem now.

For the first time, self-assembling (SA) of 1As4Ga tetrahedral clusters in AlN:(Ga, As) was considered in [4]. Such clusters are zero-dimensional ~1 nm $GaAs_{0.25}N_{0.75}$ objects embedded into the wide band gap AlN-rich matrix. Therefore, properties of 1As4Ga clusters should be close to those of ~1 nm nanocrystals with $GaAs_{0.25}N_{0.75}$ composition corresponding to the numbers of Ga–As and Ga–N bonds in AlN:(Ga, As). AlN:(Ga, As) may be the material to fabricate arrays of identical single photon emitters if excitons will form in it. As it was demonstrated, excitons form in ~1 nm CdS nanocrystals with the energy 3.5 eV which exceeds 1 eV the band gap energy of bulk CdS [5]. Thus, excitons form even in ~1 nm zero-dimensional semiconductor objects. Therefore, we can expect the formation of excitons bound to 1As4Ga clusters embedded in wide band

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gap AlN:(Ga, As). SA of similar tetrahedral clusters was described for a number of III–V and II–VI semiconductors double doped with isoelectronic impurities [6–9]. This study is devoted to SA of isoelectronic impurity clusters in triple doped semiconductors that are not considered yet. Two ensembles of identical clusters could be self-assembled in such semiconductors. Consequently, excitons with two emission energies are expected to form because of two types of clusters. Among III–V semiconductors AlN is one of the most promising candidates in which isoelectronic traps should bind excitons due to its wide band gap. Here the SA conditions of tetrahedral isoelectronic impurity clusters in AlN:(Ga, P, As), AlN:(Ga, P, Sb) and AlN:(Ga, As, Sb) are considered.

2. Theory

The SA conditions are conditions in which SA decreases the free energy of AlN:(Ga, B^V, C^V). Triple doping with Ga, B^V and C^V (B^V and C^V are phosphorus and As or phosphorus and Sb or As and Sb) transforms AlN into highly mismatched AlN-rich $Ga_xAl_{1-x}B^V{}_yC^V{}_zN_{1-y-z}$ quinary substitutional alloy of GaB^V, GaC^V, GaN, AlB^V, AlC^V and AlN. The exchange of lattice sites between cations or anions in such alloys may vary the numbers of chemical bonds. Therefore the concentrations of chemical bonds depend on the arrangement of cations and anions. Thus, the free energy of AlN-rich $Ga_xAl_{1-x}B^V{}_yC^V{}_zN_{1-y-z}$ is a sum of the free energies of the constituent compounds, strain energy and configurational entropy term $g = g^{CC} + u^{SE} - Ts^C$. Clustering or the portions of B^V and C^V atoms situated in $1B^V4Ga$ and $1C^V4Ga$ tetrahedral clusters is represented by two cluster order parameters designated α ($0 \leqslant \alpha \leqslant 1$) and β ($0 \leqslant \beta \leqslant 1$), correspondingly. We denoted $Ga_xAl_{1-x}B^V{}_yC^V{}_zN_{1-y-z}$ alloys with $\alpha = \beta = 0$ as disordered, with $0 < \alpha < 1$, $\beta = 0$ as $1B^V4Ga$ partially cluster ordered, with $0 < \alpha < 1$, $0 < \beta < 1$ as $1B^V4Ga$ and $1C^V4Ga$ partially cluster ordered, with $\alpha = 1$, $0 < \beta < 1$ as $1B^V4Ga$ completely and $1C^V4Ga$ partially cluster ordered and with $\alpha = \beta = 1$ as $1B^V4Ga$ and $1C^V4Ga$ completely cluster ordered.

The sum of the free energies of the constituent compounds is given by

$$g^{CC} = \mu_{AlN} + \Delta\mu_{B^V}xy + \Delta\mu_{C^V}xz + \Delta\mu_{B^V}\alpha(1-x)y + \Delta\mu_{C^V}\beta(1-x)z + (f_{GaN} - f_{AlN})x + (f_{AlB^V} - f_{AlN})y + (f_{AlC^V} - f_{AlN})z. \quad (1)$$

where μ_{AlN} is the chemical potential of AlN, $\Delta\mu_{B^V} = \mu_{GaB^V} - \mu_{GaN} - \mu_{AlB^V} + \mu_{AlN}$ and $\Delta\mu_{C^V} = \mu_{GaC^V} - \mu_{GaN} - \mu_{AlC^V} + \mu_{AlN}$. These relations are expressed as

$$\Delta\mu_{B^V} = \Delta h^f_{B^V} - T\Delta s_{B^V} \quad \text{and} \quad \Delta\mu_{C^V} = \Delta h^f_{C^V} - T\Delta s_{C^V},$$

where $\Delta h^f_{B^V} = h^f_{GaB^V} - h^f_{GaN} - h^f_{AlB^V} + h^f_{AlN}$, $\Delta s_{B^V} = s_{GaB^V} - s_{GaN} - s_{AlB^V} + s_{AlN}$, $h^f_{GaB^V}$ and s_{GaB^V} are the molar enthalpy of formation and entropy of GaB^V, correspondingly. Accordingly, the relations between the free energies of the constituent compounds are written as

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

$$\Delta\mu_{C^V} = \Delta h^{0f}_{C^V} - T\Delta s^0_{C^V} + \int_{298.15}^{T} \Delta c_P^{C^V} dT - T\int_{298.15}^{T} \frac{\Delta c_P^{C^V}}{T} dT$$

where $\Delta h^{0f}_{B^V} = h^{0f}_{GaB^V} - h^{0f}_{GaN} - h^{0f}_{AlB^V} + h^{0f}_{AlN}$, $\Delta s^0_{B^V} = s^0_{GaB^V} - s^0_{GaN} - s^0_{AlB^V} + s^0_{AlN}$, $\Delta c_P^{B^V} = c_P^{GaB^V} - c_P^{GaN} - c_P^{AlB^V} + s_P^{AlN}$, $h^{0f}_{GaB^V}, s^0_{GaB^V}$ are the standard enthalpy of formation and standard entropy of GaB^V, correspondingly and $c_P^{GaB^V}$ is the heat capacity of GaB^V. The change of the sum (1) under variations of the cluster order parameters depends only on $\Delta\mu_{B^V}\alpha(1-x)y + \Delta\mu_{C^V}\beta(1-x)z$. Therefore, only this part of the sum will be taken into account. The constituent compounds crystallize with the wurtzite and zinc blende structures. The difference between the enthalpies of allotropic phases of the same compound depends mainly on the co-ordination numbers, distances between the nearest atoms and Madelung constants [10]. The co-ordination numbers of the wurtzite and zinc blende structures are the same. The distances between the nearest atoms in the wurtzite and zinc blende phases are nearly equal [11]. The Madelung constants of the same compounds are almost equal. Accordingly, the difference between the enthalpies of the same wurtzite and zinc blende compounds should be insignificant. The theoretical estimates of the enthalpies of formation fulfilled in [12] also demonstrate that the enthalpies of formation of zinc blende AlN and GaN are close to those of their wurtzite analogs. The data on the standard enthalpies of formation and standard entropies and heat capacities of GaP, GaN, GaSb, AlP, AlN and AlSb are available [13]. The estimated values of the relations between the free energies of the constituent compounds $\Delta\mu_{B^V}$ and $\Delta\mu_{C^V}$ demonstrate the significant preference of AlN, GaB^V and GaC^V bonding over AlB^V, AlC^V and GaN one.

The strain energy of AlN-rich $Ga_xAl_{1-x}B^V{}_yC^V{}_zN_{1-y-z}$ is written as

$$u^{SE} = \alpha y u_{1B^V4Ga} + \beta z u_{1C^V4Ga} + (x - 4\alpha y - 4\beta z)u_{Ga} + (1-\alpha)y u_{B^V} + (1-\beta)z u_{C^V}. \quad (2)$$

where u_{1B^V4Ga}, u_{Ga} and u_{B^V} are the strain energies due to $1B^V4Ga$ cluster, isolated Ga and B^V atoms, respectively. The strain energies caused by clusters and isolated atoms were estimated as a sum of two items. The first item is the strain energy of quadruples of tetrahedral cells situated around central atoms of clusters or around isolated impurities. A quadruple of $1Ga1B^V3N$ tetrahedral cells situated around central B^V atom of $1B^V4Ga$ cluster is shown in Fig. 1. This part was described

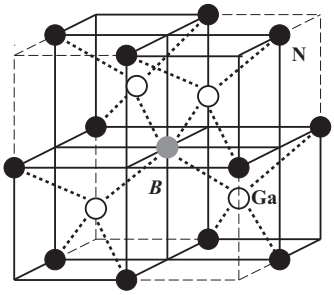

Fig. 1. Quadruple of 1Ga1B^{V}3N tetrahedral cells situated around a central B^{V} atom of 1B^{V}4Ga cluster.

by using the valence force field model and the approach developed to estimate the strain energy of III–V ternary alloys [14]. The elastic constants of bonds and angles between bonds of the constituent compounds were taken from Refs. [15,16]. The elastic constants of angles between the unlike bonds were taken as the averages of the elastic constants. The other contribution is the deformation energy of the alloy outside the quadruples. This part was represented as the energy of the elastic media with radial displacements inversely proportional to the square of a distance from the central atoms of the quadruples. The strain energies due to isolated impurities and impurity clusters were estimated as

$u_{Ga} = 2.572 \times 10^3$ [4], $u_P = 1.3535 \times 10^5$, $u_{As} = 1.7778 \times 10^5$ [4], $u_{Sb} = 2.853 \times 10^5$,
$u_{1P4Ga} = 1.6834 \times 10^5$, $u_{1As4Ga} = 2.0685 \times 10^5$ [4], $u_{1Sb4Ga} = 2.9531 \times 10^5$.

These values demonstrate the insignificant increase of the strain energy after SA.

The third item in the free energy is the configurational entropy term that was obtained as a function of the number of configurations. This number is a product of the numbers of the arrangements of anions atoms and arrangements of isolated cations at the fixed disposition of 1B^{V}4Ga and 1C^{V}4Ga clusters and anion impurities given by

$$\Omega = \Omega_1\Omega_2 = \frac{N!}{N_{B^V}!N_{C^V}!(N - N_{B^V} - N_{C^V})!} \times \frac{(N - 4\alpha N_{B^V} - 4\beta N_{C^V})!}{(N_{Ga} - 4\alpha N_{B^V} - 4\beta N_{C^V})!(N - N_{Ga})!}$$

Accordingly, the entropy term is

$$-Ts^C = -RT\ln\Omega$$
$$= RT(x - 4\alpha y - 4\beta z)\ln\frac{x - 4\alpha y - 4\beta z}{1 - 4\alpha y - 4\beta z} + RT(1 - x)\ln\frac{1 - x}{1 - 4\alpha y - 4\beta z} + RTy\ln y + RTz\ln z + RT(1 - y - z)\ln(1 - y - z).$$

The mean separation between isolated anion impurities and clusters are significantly larger then the distances between the nearest atoms. In such a case, the spatial correlations among isolated anion impurities are very small. In fact, impurity clusters and isolated impurities should be distributed randomly in the cluster ordered alloy.The values of the 1B^{V}4Ga and 1C^{V}4Ga cluster order parameters were obtained by minimizing the free energy. The SA conditions of wurtzite AlN:(Ga, B^{V}, C^{V}) should be quantitatively similar to obtained, since the thermodynamic characteristics of the wurtzite and zinc blende constituent compounds as well as their elastic constants are close.

3. Results and discussion

The Ga, B^{V} and C^{V} contents from $x = 0.005$ to $x = 0.02$ and from $y, z = 1 \times 10^{-4}$ to $y, z = 1 \times 10^{-8}$ were considered. The separations between B^{V} and C^{V} atoms at the selected contents are up to 10 nm or more. In such a case, clusters are isolated complexes. The temperature range from 0 °C to 1000 °C was used for the estimates. The temperature dependencies of the 1P4Ga and 1As4Ga cluster order parameters in $Ga_xAl_{1-x}P_yAs_zN_{1-y-z}$ with $x = 0.005$, $x = 0.01$, $x = 0.02$ and $y = 1 \times 10^{-4}$ are shown in Fig. 2. 1P4Ga and 1As4Ga cluster occurrence temperatures are equal, correspondingly, to 797 °C and 736 °C at Ga content $x = 0.02$. The temperature ranges of the partially cluster ordered alloys are very small. It allows us to choose the conditions under which the desired density of impurity clusters can be obtained. Temperatures of the SA completion are rather high as it is seen from Fig. 2. Accordingly, a thermal annealing may be used to transform a disordered alloy into cluster ordered one if disordered alloy was formed under non-equilibrium growth conditions. As it was shown the thermal annealing of GaAs-rich $In_xGa_{1-x}N_yAs_{1-y}$ epitaxial films at 600–700 °C is an efficient method of redistribution of atoms [17]. AlN-rich $Ga_xAl_{1-x}B^{V}{}_yC^{V}{}_zN_{1-y-z}$ alloys belong to the similar type of alloys as $In_xGa_{1-x}N_yAs_{1-y}$. Therefore, the thermal treatment should effectively redistribute the cation impurities on the crystal lattice sites to form impurity clusters. The SA conditions of 1As4Ga clusters shown in Fig. 2 are completely equivalent to those for AlN:(Ga, As) [18] since the temperature of an occurrence of 1P4Ga clusters in AlN:(Ga, P, As) is lower than the temperature of the SA completion of 1As4Ga clusters. The temperature dependencies of the 1P4Ga and 1Sb4Ga cluster order parameters in $Ga_xAl_{1-x}P_ySb_zN_{1-y-z}$ with $x = 0.005$, $x = 0.01$, $x = 0.02$ and $y = z = 1 \times 10^{-4}$ are shown in Fig. 3. The 1P4Ga and 1Sb4Ga cluster occurrence temperatures are equal,

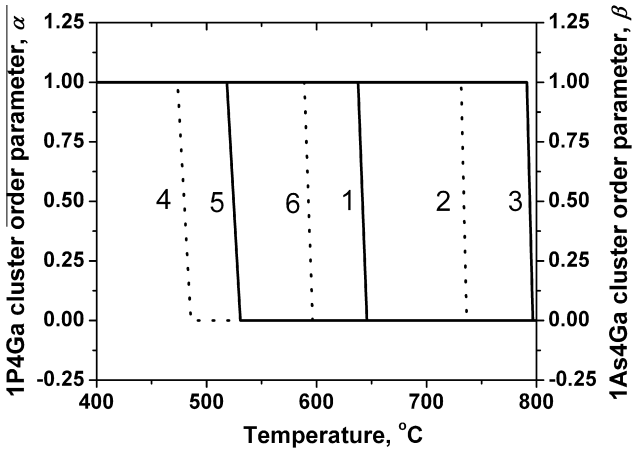

Fig. 2. The temperature dependencies of the 1P4Ga (solid curves) and 1As4Ga (dotted curves) cluster order parameters in AlN:(Ga, P, As): $Ga_xAl_{1-x}B^V_yC^V_zN_{1-y-z}$, $y = z = 0.001$ (curves 1, 4. $x = 0.005$; curves 2, 5. $x = 0.01$; curves 3, 6: $x = 0.02$).

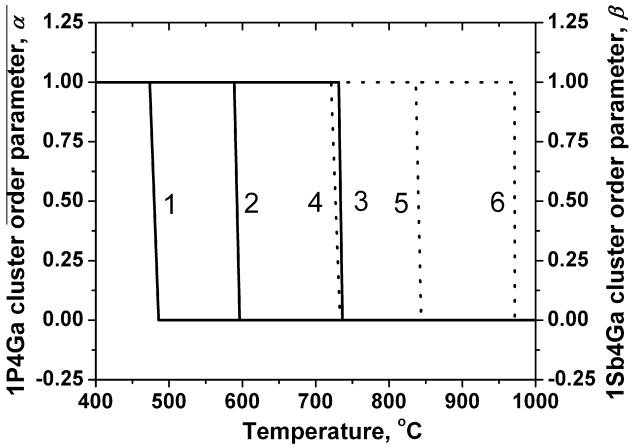

Fig. 3. The temperature dependencies of the 1P4Ga (solid curves) and 1Sb4Ga (dotted curves) cluster order parameters in AlN:(Ga, P, Sb): $Ga_xAl_{1-x}B^V_yC^V_zN_{1-y-z}$, $y = z = 0.001$ (curves 1, 4. $x = 0.005$; curves 2, 5. $x = 0.01$; curves 3, 6: $x = 0.02$).

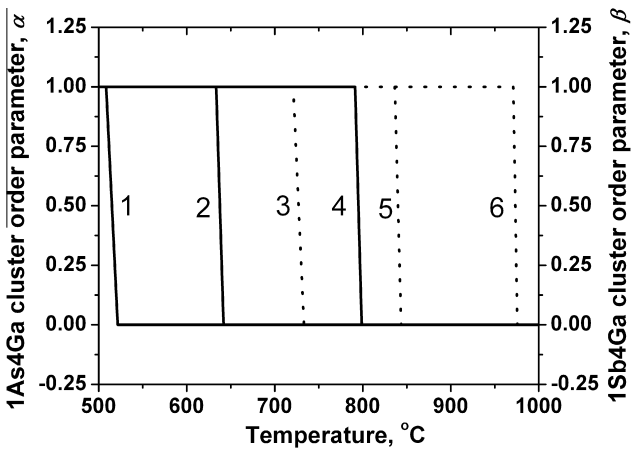

Fig. 4. The temperature dependencies of the 1As4Ga (solid curves) and 1Sb4Ga (dotted curves) cluster order parameters in AlN:(Ga, As, Sb): $Ga_xAl_{1-x}B^V_yC^V_zN_{1-y-z}$, $y = z = 0.001$ (curves 1, 4. $x = 0.005$; curves 2, 5. $x = 0.01$; curves 3, 6: $x = 0.02$).

correspondingly, to 976 °C and 736 °C at $x = 0.02$. The SA conditions of 1Sb4Ga clusters shown in Fig. 3 are completely equivalent to those calculated for AlN:(Ga, Sb) since the temperature of an occurrence of 1P4Ga clusters is lower than the temperature of the SA completion of 1Sb4Ga clusters. The temperature dependencies of the 1As4Ga and 1Sb4Ga cluster order parameters in $Ga_xAl_{1-x}As_ySb_zN_{1-y-z}$ with $x = 0.005$, $x = 0.01$, $x = 0.02$ and $y = z = 1 \times 10^{-4}$ are shown in Fig. 4. The SA conditions of 1Sb4Ga clusters are also completely equivalent to those estimated for AlN:(Ga, Sb). The temperature dependencies of the cluster order parameters shown in Figs. 2–4 demonstrate that an occurrence of clusters and SA completion are the results of the continuous phase transitions. The 1As4Ga and 1Sb4Ga cluster occurrence temperatures are equal to those for AlN:(Ga, P, As) and AlN:(Ga, P, Sb), correspondingly, at $x = 0.02$. The results shown in Figs. 2–4 demonstrate that SA of 1P4Ga 1As4Ga and 1Sb4Ga clusters in AlN:(Ga, P, As), AlN:(Ga, P, Sb) and AlN:(Ga, As, Sb) is thermodynamically preferential in the wide temperature and impurity content ranges.

4. Conclusions

To conclude, the self-assembling conditions of the identical tetrahedral clusters of two types in AlN:(Ga, P, As), AlN:(Ga, P, Sb) and AlN:(Ga, As, Sb) are obtained. AlN:(Ga, P, As), AlN:(Ga, P, Sb) and AlN:(Ga, As, Sb) are quinary AlN-rich alloys containing six types of chemical bonds. The preferable formation of three types of bonds leads to self-assembling in the wide temperature and impurity content ranges. A cluster occurrence and self-assembling completion when all one type anion impurities are in clusters should be in the narrow temperature ranges. These results demonstrate that AlN:(Ga, P, As), AlN:(Ga, P, Sb) and AlN:(Ga, As, Sb) are promising candidates to obtain arrays of identical $\sim$1 nm low band gap zero-dimensional objects of two types in the wide band gap semiconductor matrix.

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