Tetrahedral 1B4Sb nanoclusters in GaP:(B, Sb)

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Abstract. Self-assembling conditions of 1B4Sb tetrahedral nanoclusters in GaP doped with boron and Sb isoelectronic impurities are represented in the ultradilute and dilute limits of the boron and Sb contents, respectively. The fulfilled estimates demonstrated the preferential complete or almost complete allocation of boron atoms in 1B4Sb nanoclusters at temperatures of 500 °C and 900 °C, respectively. The significant decrease of the sum of the free energies of the constituent compounds is the main origin of self-assembling. The reduction of the strain energy is the additional cause of this phenomenon.

1. Introduction

Self-assembling (SA) of 1N4Al and 1As4Ga tetrahedral nanoclusters in GaAs:(Al, N) and zinc blende AlN:(Ga, As), respectively, was predicted in Ref. [1]. The co-doping of a binary compound BD with cation A and anion C isoelectronic impurities transforms it into $A_{x}B_{1-x}C_{y}D_{1-y}$ quaternary alloy. In these alloys an exchange of lattice sites between cations or anions leads to the reaction between bonds $nA-C+nB-D \rightarrow nA-D+nB-C$ ($1 \leq n \leq z$, where $z$ is a coordination number). The larger sum of the cohesive energies of the bonds participating in the reaction provides their preferential formation. A decrease of the strain energy after SA is an additional cause of the impurity complex formation in such alloys. The main origin of SA in GaAs:(Al, N) and AlN:(Ga, As) is a preferential AlN and GaAs bonding over AlAs and GaN one. The equality conditions of the free energies of the random alloys and alloys in which all minority impurities are in the nanoclusters were represented [1]. Later the phase diagram of AlN:(Ga, As) with the partial location of minority impurities in the nanoclusters was developed [2].

Size dispersion is the main problem of the semiconductor structures with the zero-dimensional nanoobjects such as quantum dots. A technology of the monodisperse quantum dots is not developed yet. SA of the boron and Sb isoelectronic impurity nanoclusters is proposed as a line of attack on this problem that is the formation of monodisperse semiconductor nanoobjects embedded in the wide gap matrix. GaP:(B, Sb) is proposed as a semiconductor with 1B4Sb nanoclusters. One of the reason of SA in GaP:(B, Sb) can be a decrease of the lattice strains after the formation of 1B4Sb nanoclusters from isolated atoms. The tetrahedral covalent radii of boron and Sb are smaller and larger than those of Ga and phosphor, respectively. Isolated boron and Sb atoms dilate and shrink, respectively, a crystal lattice of GaP:(B, Sb). The dilation and shrinking compensate each other after SA of 1B4Sb nanoclusters. Thus, SA is preferential from the strain energy standpoint. GaP:(B, Sb) is a GaP-rich $B_{x}Ga_{1-x}Sb_{y}P_{1-y}$ alloy. Moreover, in such alloy an exchange of lattice sites between
cations or anions alters the quantities of bonds according to the reaction $nGa-Sb + nB-P \rightarrow nGa-P + nB-Sb$ ($n = 1,\ldots,4$) or vice versa. The larger sum of the cohesive energies of bonds participating in the reaction provides their preferential formation. It can be an additional reason of the SA. The nanocluster may be represented as a quantum dot with a size of the order of 1 nm and with the composition $Ga_{0.75}B_{0.25}Sb$ that is determined by Ga-Sb and B-Sb bonds in the wide band gap GaP-rich alloy. The SA conditions in the binary semiconductor compounds co-doped with the cationic and anionic isoelectronic impurities are represented by the phase diagrams [2]. The aim of the paper is to consider a phase diagram of GaP:(B, Sb).

2. The Model

The free energy of a GaP-rich $B_xGa_{1-x}Sb_yP_{1-y}$ cluster ordered alloy $f = h^0 + u_{SE} - TS_C$ is as a sum of the enthalpies of the constituent compounds $h^0$, strain energy $u_{SE}$ and configurational entropy term $-TS_C$. The clustering degree is represented by the cluster order parameter $\alpha$ that is a fraction of boron atoms situated in 1B4Sb nanoclusters. This parameter can vary from zero to unity. The alloys with $\alpha = 0$, $0 < \alpha < 1$ and $\alpha = 1$ are homogeneous, partially cluster ordered and completely cluster ordered ones, respectively [2]. The ultradilute and dilute limits for the boron and Sb contents, respectively, are considered. The arrangement of boron atoms should be random and this fact is taken into account when describing the items of the sum. The sum of the enthalpies of the constituent compounds is given as

$$
n^0 = xh^0_{BSb} + x(1-y)h^0_{BP} + (1-x)yh^0_{GaSb} + (1-x)(1-y)h^0_{GaP} + \alpha(1-x)y(h^0_{BSb} - h^0_{BP} - h^0_{GaSb}) + \alpha h^0_{GaP},
$$

where $x$ and $y$ are the concentrations of boron and Sb in the cation and anion sublattices, respectively. The variation of the sum (1) as a result of SA depends on the relation $h^0_{BSb} - h^0_{BP} - h^0_{GaSb} + h^0_{GaP}$. Therefore, only last item of the sum (1) should be taken into account. The value of this relation is equal to the similar relation between the enthalpies of formation. The enthalpies of formation of BP, GaSb and GaP are available [3]. The enthalpy of formation of Bsb was obtained from the cohesive energy of Bsb and atomization energies of boron and Sb as

$$
\Delta f_{BSb} = u_{BSb} + u_{B} - u_{Sb}.
$$

The atomization energies were taken from [4]. The cohesive energy of Bsb was estimated by the Sanderson's theory [4] as a sum of the ionic and covalent components that are given as

$$
uu_{BSb} = \frac{1.39M_{BSb}(R_B + R_{Sb})k}{R_{BSb}}t_i + 4.19 \times 10^{-3}(R_B + R_{Sb})\sqrt{u_Bu_{Sb}}(1 - t_i) = 0.185 \text{ MJ/mole},
$$

where $M_{BSb}$ is the Madelung constant of Bsb, $R_B$ and $R_{Sb}$ are the covalent radii of boron and Sb, respectively, $k$ is the repulsion coefficient, $t_i$ is the average of the partial charges on two atoms forming B-Sb bond, $R_{BSb} = 0.516 \text{ nm}$ [5] is the distance between the nearest atoms in Bsb, $u_B$ and $u_{Sb}$ are the atomization energies of boron and Sb, respectively. The obtained value of the relation between the enthalpies of formation $h^0_{BSb} - h^0_{BP} - h^0_{GaSb} + h^0_{GaP} = -1.502 \times 10^5 J/\text{mole}$ demonstrates the significant preferential B-Sb and Ga-P bond formation over the B-P and Ga-Sb one.

The strain energy of the GaP-rich $B_xGa_{1-x}Sb_yP_{1-y}$ alloy is given as

$$
uu_{SE} = xu_B + yu_{Sb} + \alpha y(u_{B4Sb} - u_B - 4u_{Sb}),
$$

where $u_{B4Sb}$, $u_B$ and $u_{Sb}$ are the strain energies caused by the impurity nanoclusters and isolated impurities, respectively. As it is seen from (2) the strain energy does not depend on the clustering degree since the relation $y >> x$ is fulfilled. The strain energies caused by nanoclusters 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 the central atoms of nanoclusters or around isolated boron and Sb.
impurities. This part was described using the valence force field model by the approach developed for the strain energy estimation of III-V ternary alloys [6]. The averages of the bond bending elastic constants of the compounds were used as elastic constants of the angles between the unlike bonds. The bond stretching and bond bending elastic constants of GaSb and GaP were taken from [7]. The bond stretching and bond bending elastic constants of BSb and BP were estimated by the valence force field model [7] using the stiffness coefficients taken from [8] and [9], respectively. 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 caused by isolated boron and Sb atoms and 1B4Sb nanoclusters are equal, respectively, to 

\[ u_B = 1.017 \times 10^5 \text{ J/mole}, \quad u_{Sb} = 1.215 \times 10^5 \text{ J/mole} \]

and 

\[ u_{1B4Sb} = 1.189 \times 10^5 \text{ J/mole}. \]

Thus, SA of 1B4Sb nanoclusters reduces almost five times the strain energy and this fact also demonstrates the significant B-Sb and Ga-P bond preferential formation over the B-P and Ga-Sb one.

The third item is given as

\[
-T_{sc} = RT \left[ x \ln x + (1-x) \ln(1-x) + (y-4\alpha x) \ln \frac{y-4\alpha x}{1-4\alpha x} + (1-y) \ln \frac{1-y}{1-4\alpha x} \right].
\] (3)

The number of configurations was considered as a product of two factors. The first one is a number of arrangements of the cations. There is a random distribution of the cations because of the chosen ultradilute limit for the boron content. The second one is a number of the arrangements of anions situated outside 1B4Sb nanoclusters at the fixed allocation of isolated boron atoms and nanoclusters. The mean distances between isolated boron atoms and 1B4Sb nanoclusters are significantly larger then those between the nearest atoms. In such a case, spatial correlations among boron atoms that are outside nanoclusters are very small. In fact, impurity nanoclusters and isolated boron atoms should be distributed randomly in the cluster ordered alloy.

3. Results and Discussion

The boron and Sb contents \(10^{-8} \leq x \leq 10^{-4}\) and \(4x \leq y \leq 10^{-2}\), respectively, were considered. The ultradilute limit for the boron concentration was chosen in order to avoid the interactions between nanoclusters. In such a case nanoclusters should create bound states. In the case of the dilute limits the formation of nanoclusters will change the band gap. GaP and GaP-rich alloys are mainly grown by the metalorganic chemical vapor deposition at temperatures of 500 °C and 900 °C if tertiarybutylphosphine and phosphine are used, respectively, as precursors of phosphor. Therefore, the temperature range between these temperatures was chosen for the estimates. The clustering degree is determined by the condition \( \frac{df}{d\alpha} = 0 \) [2]. The fulfilled estimates demonstrated that at temperature of 500 °C the preferential thermodynamically phase state should be the completely cluster ordered (\( \alpha = 1 \)) in the entire boron content range and at the Sb content \( y \geq 4x \). At higher temperature of 900 °C only negligibly small fraction of boron atoms (1 - \( \alpha < 0.001 \)) are isolated in the entire boron content range and at the Sb content \( y \geq 4x \). Thus, at both considered temperatures the alloys should be the completely cluster ordered or almost completely cluster ordered phase ones. In comparison with the alloys such as zinc blende AlN-rich Ga\(_a\)Al\(_{1-x}\)As\(_{1-y}\), ZnTe-rich Mg\(_{1-x}\)Zn\(_{1+y}\)O\(_{2+y}\)Te\(_{1-y}\) and ZnTe-rich Sr\(_{1-x}\)O\(_{2+y}\)Te\(_{1-y}\) [2; 10-11] GaP-rich B\(_x\)Ga\(_{1-x}\)Sb\(_{1-y}\) alloys demonstrate the larger cluster ordering.

The bond composition of 1B4Sb nanoclusters corresponds to B\(_{0.25}\)Ga\(_{0.75}\)Sb alloy. The bandgap of such alloy should be smaller than that of GaP since the bandgap of BSb is smaller than that of GaSb [12]. Thus, 1B4Sb nanoclusters in GaP-rich B\(_x\)Ga\(_{1-x}\)Sb\(_{1-y}\) alloy are zero-dimensional uniform narrow bandgap objects in wide bandgap semiconductor.

4. Conclusions

The self-assembling conditions of 1B4Sb nanoclusters in GaP:(B, Sb) were obtained in the ultradilute boron and dilute Sb limits. The decrease of the free energy contribution of the constituent compounds
and reduction of the strain energy after the formation of 1B4Sb nanoclusters are origins of self-assembling. The transformation of B-P and Ga-Sb bonds into more preferential B-Sb and Ga-P ones and decrease of the strain energy are the origins of self-assembling. In the considered concentration ranges all or almost all boron atoms should be in 1B4Sb nanoclusters at temperatures of 500 °C and 900 °C, respectively.

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