B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32} three-dimensional semiconductor superlattice

Vyacheslav A. Elyukhin1 · Ramon Peña Sierra1

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Abstract
Self-assembly of BD-rich A_{x}B_{1−x}C_{y}D_{1−y} was studied for a lot of semiconductor alloys. An occurrence of identical clusters should be due to a decrease of the bond energy, internal strain energy or both of them. An arrangement of clusters is disordered since the contents of minority atoms are in the dilute or ultra dilute limits in the considered alloys. B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32} semiconductor alloy with the three-dimensional superlattice is presented. Such superlattice should be stable against disordering due to its minimal free energy. The superlattice is formed by the identical cubic units consisting of 64 atoms and is the three-dimensional semiconductor soft X-ray diffraction grating.

Keywords Semiconductors · Quaternary alloy · Superlattice · Diffraction grating

1 Introduction
Crystal engineering is one of the pathways to extend the class of semiconductors for device applications. The design of solid state structures seems promising for polyatomic materials due to their larger variance. The III–V quaternary semiconductor alloys with the crystal structure having two mixed sublattices are long ago and successfully used for fabrication of the optoelectronic devices (Hsieh et al. 1976; Hurwitz and Hsieh 1978). One of the structural peculiarities of such alloys is the short-range order (SRO) or non-random arrangement of cations and anions in their sublattices that, for the first time, was established for In_{x}Ga_{1−x}As_{y}P_{1−y} alloys (Iveronova and Sapkova 1979). SRO is caused by the bond energy and internal strains depending on the atomic location (Elyukhin et al. 1982; Onabe 1982). The non-random distribution of atoms leads to an occurrence of different clusters situated randomly. Almost exclusive formation of complexes with the AlN bonding was observed in Al_{x}Ga_{1−x}N_{y}As_{1−y} alloys with x ≤ 0.05 and y ≤ 0.04 (Geppert et al. 2002). Al_{x}Ga_{1−x}N_{y}As_{1−y} are alloys with the highly mismatched anions but the cations have almost the same size. Therefore, the redistribution of cations may change the bond energy only. The complexes with the AlN bonding should be clusters with one nitrogen atom. The formation of clusters
with two or more nitrogen atoms is improbable since it will increase significantly the internal strains.

The 1N4Al and 1As4Ga identical clusters formation was considered for GaAs-rich 
\[
\text{Al}_x\text{Ga}_{1-x}\text{N}_y\text{As}_{1-y}
\]
and AlN-rich \( \text{Ga}_x\text{Al}_{1-x}\text{As}_y\text{N}_{1-y} \) \((x>4y)\) alloys, respectively (Elyukhin et al. 2004). The GaAs- and AlN-rich alloys are the alloys of four binary compounds AlN, AlAs, GaN and GaAs corresponding to the bonding in them. In such alloys redistribution of cations or anions in their sublattices may result in the transformation of pairs of chemical bonds: 
\[
n(\text{Al-N}) + n(\text{Ga-As}) \rightarrow n(\text{Al-As}) + n(\text{Ga-N}) \quad (n = 1,\ldots,4)
\]
or vice versa. The 1N4Al and 1As4Ga clusters formation should be due to the fact that the AlN and GaAs bonding is favorable over the AlAs and GaN bonding. The 1O4Sr cluster formation conditions in ZnTe-rich \( \text{Sr}_x\text{Zn}_{1-x}\text{O}_y\text{Te}_{1-y} \) highly mismatched alloys were presented in Elyukhin (2008). Sr and oxygen atoms are larger and smaller, respectively, than Zn and Te atoms. Therefore, the occurrence of 1O4Sr clusters in \( \text{Sr}_x\text{Zn}_{1-x}\text{O}_y\text{Te}_{1-y} \) decreases the internal strains. The detailed description of the 14A4C identical cluster formation conditions in BD-rich \( A_x\text{B}_{1-x}\text{C}_y\text{D}_{1-y} \) semiconductor alloys is in Elyukhin (2016).

The concurrent 1B4Sb and 4B10Sb clusters formations in GaAs-rich \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) alloys were considered in Elyukhin (2011). 1B4Sb and 4B10Sb clusters are Sb tetrahedrons with boron atoms in their centers and boron tetrahedrons surrounded by Sb atoms, respectively. The favorable BSb and GaAs bonding over the BAs and GaSb bonding is the first cause of the cluster occurrence. Boron and Sb atoms are smaller and larger than Ga and As atoms, respectively. Therefore, the cluster occurrence considerably compensates the internal strains caused by boron and Sb isolated atoms. The decrease of the internal strains is the second cause of the clusters formation. 4B10Sb and 1B4Sb clusters form the nanoscale order due to their random distribution in the GaAs-rich matrix (Elyukhin 2011). In addition, the 4B10Sb cluster density should be significantly larger than that of 1B4Sb clusters.

The studied alloys with the identical clusters do not have the superlattices. Apparently, a superlattice may be expected in the quaternary alloys with other atomic contents. Among the considered alloys, the identical cluster formation is more favorable in GaAs-rich \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) alloys. Therefore, the possible types of superlattices in \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) seem most likely. Moreover, the stability against disordering should be also studied to determine suitability of the superlattice for device applications. The \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) superlattice stable against disordering is presented here.

### 2 Model

The 4B10Sb and 1B4Sb clusters formation decrease the bond and internal strain energies of GaAs-rich \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) alloys (Elyukhin 2011). Diminutions of the bond energy due to the cluster formation are the same for both types of the clusters since all boron atoms are surrounded by Sb atoms and form B-Sb chemical bonds. The internal strain energies produced by isolated boron and Sb atoms as well as 1B4Sb clusters in the GaAs-rich \( B_x\text{Ga}_{1-x}\text{Sb}_y\text{As}_{1-y} \) alloys are available (Elyukhin 2009). The internal strain energy caused by 4B10Sb clusters is calculated as a sum of the deformation energies produced by 4B10Sb clusters and GaAs-rich matrix is 
\[
u_{\text{4B10Sb}} + \nu_{\text{GaAs}} = 87.498 \text{ kJ mol}^{-1}
\]

The deformation energy (87.782 kJ mol\(^{-1}\)) obtained in Elyukhin (2011) is insignificantly overestimated. The overestimation is due to the supposition on the unstrained GaAs-rich matrix. The estimated deformation energy of the GaAs-rich matrix is only 3% of the total internal strain.
energy produced by $4B10Sb$ clusters. Thus, the GaAs-rich matrix is weakly strained. The decrease of the internal strain energy is almost two times larger after the $4B10Sb$ cluster formation than that after the $1B4Sb$ one. Therefore, a superlattice containing $4B10Sb$ clusters is considered and should be a set of identical units. Moreover, the set should also have the maximal fraction of B-Sb and Ga-As bonds since they are favorable over B-As and Ga-Sb bonds. The period of the zinc blende structure in the <001> directions is equal to distance between 4 atomic layers. However, $4B10Sb$ cluster (shown in Fig. 1) is in 5 (001) oriented atomic layers. Therefore, the minimal unit of a superlattice cannot be less than in 8 (001) atomic layers (2 lattice parameters of the zinc blende structure). Thus, except $4B10Sb$ cluster, the additional atomic layers filled by Ga and As atoms should be in the unit.

There are 6 variants of such units with atoms in 8 atomic layers in the {001} oriented planes due to the different positions of As atomic layers. One of these variants is shown in Fig. 2.

$4B10Sb$ cluster is shown by red lines. In accordance with Fig. 2, the atomic layers are filled by the next way: 8 Ga (1th layer); 5As, 3Sb (2nd layer); 6 Ga, 2B (3d layer); 4As, 4Sb (4th layer); 6 Ga, 2B (5th layer); 5As, 3Sb (6th layer); 8 Ga (7th layer); 8 As (8th layer). Such units consisting of 64 atoms form $B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32}$ alloy with the superlattice. The superlattice should consist of the units having the same position of $4B10Sb$ clusters. The set consisting of the units with the different positions of the clusters is non-profitable from the bond energy standpoint due to the increase of the quantities of non-favorable Ga-Sb and B-As chemical bonds.

3 Results and discussion

$B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32}$ superlattice is the semiconductor three-dimensional soft X-ray diffraction grating with period $2^{3/2}d_{GaAs} = 1.598$ nm in the <001> directions, period $2^2d_{GaAs} = 2.260$ nm in the <011> directions and period $3^{1/2}2^{3/2}d_{GaAs} = 2.768$ nm in the <111> directions, where $d_{GaAs}$ is the lattice parameter of GaAs. The superlattice
is almost lattice matched to GaAs and, therefore, may be grown on the GaAs substrates. However, the stability against disordering should be studied to establish possibility of the practical applications. To describe the disordering processes, the Ga (As) and boron (Sb) lattice sites are considered. The Ga (As) and boron (Sb) sites are the lattice sites on which are Ga (As) and boron (Sb) atoms, respectively, in the superlattice. The transitions of boron and Ga atoms from the boron and Ga sites to the Ga and boron sites are the cationic disordering processes. The other disordering processes are the transitions of Sb and As atoms from the Sb and As sites to the As and Sb sites (anionic processes). Such cationic and anionic processes increase the bond energy since they decrease the quantities of B-Sb and Ga-As bonds and, accordingly, increase the quantities of B-As and Ga-Sb bonds. However, these processes increase the entropy.

The cationic disordering processes are considered as follows. The exchanges of boron and Ga atoms between the nearest sites in the cationic sublattice are taking into account. There is one type of the boron sites since each boron atom in the superstructure is surrounded by only Sb atoms. The Ga sites participating in the processes are also the same from the bond energy standpoint as each Ga atom forms one Ga-Sb bond. After the exchange of the lattice sites boron atom should be on one of the 9 nearest Ga sites. The atomic unit has 24 nearest Ga sites for boron atoms (Fig. 1). The total number of Ga atoms in one unit is 28. The transformation of bonds as a result of the disordering process is

\[
3 \text{B-Sb} + 3 \text{Ga-As} \rightarrow 3 \text{B-As} + 3 \text{Ga-Sb}
\]

The increase of the bond energy after this bond transformation is \(2.314 \times 10^{-19}\) J. There are two types of the Sb sites in completely ordered \(B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32}\) superlattice. There are 6 Sb sites with two B-Sb bonds and 4 Sb sites with one B-Sb bond in the unit (Fig. 1). All As sites are the same since they surrounded by only the Ga sites. Therefore, two different anionic disordering processes should be considered. The first anionic process is the exchange such that the transformation of bonds is

\[
2 \text{B-Sb} + 2 \text{Ga-As} \rightarrow 2 \text{B-As} + 2 \text{Ga-Sb}
\]

In this process may participate 60% Sb atoms. Each of 60% Sb atoms may be allocated on 10 As sites. The increase of the bond energy after this bond transformation is \(1.542 \times 10^{-19}\) J. The second variant of the anionic processes is accompanied by bond transformation \(B_{4/32}Ga_{28/32}Sb_{10/32}As_{22/32}\) increasing the bond energy by \(7.713 \times 10^{-20}\) J. Moreover, all disordering processes increase the internal strain energy.

Fig. 2 Atomic layers in the cubic unit. The numbers of atomic layers are shown in the brackets.
Any disordering processes increase the entropy and, therefore, these increases of the entropy term should be taken into account to estimate the variation of the free energy. There are one disordering process for cations and two processes for anions, in accordance with the transformations of the chemical bonds. They are the exchange of the lattice sites between the nearest cations and between the nearest anions. There are 4 boron atoms in the unit. Each boron atom has 9 nearest Ga atoms and 3 nearest boron atoms in the cationic sublattice. Thus, each boron atom may be on one of 9 Ga sites after the exchange of the lattice sites. As a result, the entropy term increases by $T \Delta s = 7.181T \times 10^{-22}$ J mol$^{-1}$ and is $2.154 \times 10^{-19}$ J mol$^{-1}$ at RT. There are two types of the Sb sites corresponding to the reactions transforming chemical bonds:

1. $2 \text{B-Sb} + 2 \text{Ga-As} \rightarrow 2 \text{B-As} + 2 \text{Ga-Sb}$ and 2. $\text{B-Sb} + \text{Ga-As} \rightarrow \text{B-As} + \text{Ga-Sb}$. Accordingly, two additional changes of the entropy terms should be estimated. In the case of the reaction between pairs of bonds there are 6 Sb atoms with reaction 1 (6 nearest As sites for 1 Sb atom) and 4 Sb atoms with reaction 1 (9 nearest As sites for 1 Sb atom) in the unit. The increase of the entropy term is $T \Delta s = 7.181T \times 10^{-22}$ J mol$^{-1}$ and is $2.154 \times 10^{-19}$ J mol$^{-1}$ at RT. There are 4 Sb atoms for bond reaction 2: $\text{B-Sb} + \text{Ga-As} \rightarrow \text{B-As} + \text{Ga-Sb}$. The increase of the entropy term is $T \Delta s = 7.181T \times 10^{-22}$ J mol$^{-1}$ and the increase is also equal to $2.154 \times 10^{-19}$ J mol$^{-1}$ at RT. The amounts of $\text{B}_{4/32}\text{Ga}_{28/32}\text{Sb}_{10/32}\text{As}_{22/32}$ films grown on the GaAs lattice matched substrates, normally, should be significantly smaller than one mole. Therefore, the $\text{B}_{4/32}\text{Ga}_{28/32}\text{Sb}_{10/32}\text{As}_{22/32}$ completely ordered superlattice has to be stable against the disordering processes.

### 4 Conclusions

To conclude, $\text{B}_{4/32}\text{Ga}_{28/32}\text{Sb}_{10/32}\text{As}_{22/32}$ highly mismatched alloy with the completely ordered superlattice is favorable from the thermodynamics standpoint. Any disordering process should increase the free energy. Accordingly, the completely ordered superlattice is stable against disordering. Such superlattice is the semiconductor three-dimensional soft X-ray diffraction grating consisting of the identical cubic 64 atomic units.

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### Authors contribution

Conceptualization: [VAE]; Methodology: [VAE]; Writing: original draft preparation: [VAE]; Calculations: [RP]; Writing—review and editing: [RPS].

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