Superlattices and Microstructures 80 (2015) 32–38

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Self-assembling of In and nitrogen in GaP:(In, N)

V.A. Elyukhin *

Departamento de Ingeniería Eléctrica-SEES, CINVESTAV-IPN, México, D.F., C.P. 07360, Mexico

ARTICLE INFO

Article history:
Received 23 December 2014
Accepted 26 December 2014
Available online 3 January 2015

Keywords:
Semiconductors
Isoelectronic impurities
Self-assembling
Identical clusters

ABSTRACT

Highly mismatched GaP:N attracts now considerable interest in fabricating ensembles of single photon sources. Significant reduction of undesirable internal strains around nitrogen atoms can be achieved by additional doping with In due to self-assembling of 4N10In and 1N4In clusters in GaP:(In, N). Double doping transforms GaP into GaP-rich $In_xGa_{1-x}N_yP_{1-y}$ substitutional alloy of InN, InP, GaN and GaP. Self-assembling of clusters results in the decrease of the sum of the free energies of the constituent compounds and strain energy. The self-assembling conditions are considered from 0 °C to 1000 °C in the dilute and ultra dilute limits for In and nitrogen impurities, respectively. Almost all nitrogen atoms are in 4N10In clusters over the entire temperature range if $x = 1 \times 10^{-3}$, $y = 1 \times 10^{-4}$; $x = 1 \times 10^{-4}$, $y = 1 \times 10^{-5}$ and $x = 1 \times 10^{-5}$, $y = 1 \times 10^{-6}$. Both types of clusters with considerable densities are in GaP-rich $In_xGa_{1-x}N_yP_{1-y}$ if the ratio between the In and nitrogen contents is 100. If this ratio is ≈1000 then all nitrogen impurities are in 1N4In clusters over the entire temperature range. The fulfilled estimates demonstrate that GaP:(In, N) is a promising candidate to fabricate ensembles of single photon sources due to small strains around nitrogen atoms in 4N10In and 1N4In clusters.

1. Introduction

Ensembles of single photon sources with high optical homogeneity are strongly required to fabricate quantum computers which should considerably improve computational power [1]. In the last few years, GaP:N is studied as one of the semiconductors suitable for such ensembles formation [2,3].

* Tel.: +52 5747 3773.
E-mail address: elyukhin@cinvestav.mx

http://dx.doi.org/10.1016/j.spmi.2014.12.026
0749-6036/

Isolated nitrogen atoms and nitrogen dyads bound excitons in GaP:N as it was established in the middle of 1960s [4,5]. Isolated nitrogen atoms form very shallow exciton traps in this semiconductor but the dyads result in deep exciton traps with the binding energy that increases with a decrease of the separation between impurities. Moreover, the nitrogen triads also form exciton traps in this material that are significantly deeper than those formed by isolated nitrogen impurities [6].

Nitrogen is a highly mismatched isoelectronic impurity in GaP. However, in spite of this, GaP:N is GaP-rich GaN_yP_{1-y} substitutional alloy. Due to the high mismatch the nitrogen concentrations in GaP:N should be significant in order to obtain desired density of nitrogen dyads and triads. Therefore, the δ-doping providing considerable nitrogen concentration as well as significant internal strains in a thin layer is used in the epitaxial growth of GaP:N [2,3]. These strains cause an inadmissible inhomogeneity in the emission energy of the excitons bound to the impurity complexes. That is why, a search of the ways to create the GaP-rich semiconductors with exciton traps lying in the reduced strain fields is important to produce ensembles of the identical single photon sources.

Self-assembling (SA) of identical isoelectronic impurity clusters can be one of the ways to resolve this problem. It was found that SA of 4B10Sb and 1B4Sb clusters reduces considerably the internal strains in GaP:(B, Sb) [7]. 4B10Sb clusters are empty boron tetrahedrons surrounded by Sb impurities and boron atoms in 1B4Sb clusters are in the centers of Sb tetrahedrons. SA of such clusters compensates considerably the dilation and shrinking of the crystal lattice due to isolated boron and Sb atoms, respectively. The reduction of the internal strain energy is one of the reasons of SA. Moreover, double doping with boron and Sb transforms GaP into GaP-rich $B_xGa_{1-x}Sb_yP_{1-y}$ substitutional alloy of BSb, BP, GaSb and GaP. An exchange of lattice sites between cations or anions in this alloy leads to the reaction between bonds: nB-Sb + nGa-P $\rightarrow$ nB-P + nGa-Sb, (n = 1,. . ., z) or vice versa, where z is the co-ordination number. BSb and GaP bonding is thermodynamically preferable over that of BP and GaSb. SA of 4B10Sb and 1B4Sb clusters increases B-Sb and Ga-P bond concentrations and decreases B-P and Ga-Sb bond concentrations. Thus, the increase of the quantities of B-Sb and Ga-P bonds is the second reason of SA.

Similarly, double doping with In and nitrogen transforms GaP into GaP-reach $In_xGa_{1-x}N_yP_{1-y}$ substitutional alloy of InN, InP, GaN and GaP. Isolated In and nitrogen impurities, consequently, shrink and dilate the crystal lattice of $In_xGa_{1-x}N_yP_{1-y}$. SA of 4N10In and 1N4In clusters in GaP:(In, N) as well as SA of 4B10Sb and 1B4Sb clusters in GaP:(B, Sb) should decrease the internal strain energy due to the compensation of the shrinking and dilation since the covalent radii of In and nitrogen are larger and smaller than those of Ga and phosphorus, correspondingly. Moreover, InN and GaP bonding is thermodynamically preferable over that of InP and GaN. Thus, in GaP:(In, N) there are also two causes for SA of 4N10In and 1N4In clusters. The SA conditions of In and nitrogen in GaP:(In, N) are studied here.

2. Theory

4N10In and 1N4In clusters shown in Figs. 1 and 2, correspondingly, should occur in GaP:(In, N) if SA decreases the Helmholtz free energy. The free energy of GaP co-doped with In and nitrogen or GaP-rich $In_xGa_{1-x}N_yP_{1-y}$ substitutional alloy is a sum of three items $g = g^0 + u - Ts$, where g^0 is a sum of the free energies of constituent compounds InN, InP, GaN and GaP, u is the strain energy and $-Ts$ is the configurational entropy term. The 4N10In and 1N4In clustering degrees are represented by 4N10In cluster order parameter (4N10In COP) α and 1N4In cluster order parameter (1N4In COP) β. The parameters are ratios between the numbers of nitrogen atoms in 4N10In and 1N4In clusters and total number of nitrogen atoms.

The sum of the free energies of the constituent compounds is

$$g^0 = \Delta\mu^0(\alpha+\beta)(1-x)y + \Delta\mu^0 xy + \mu^0_{GaP} + (\mu^0_{InP} - \mu^0_{GaP})x + (\mu^0_{GaN} - \mu^0_{GaP})y, \quad (1)$$

where $\Delta\mu^0 = \mu^0_{InN} - \mu^0_{InP} - \mu^0_{GaN} + \mu^0_{GaP}$ and μ^0_{InN} is the free energy 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 later on. The relation between the free energies is given by

$$\Delta\mu^0 = \Delta h^0 - T\Delta s,$$