

Model of annealing-induced short-range order effects in (GaIn)(NP) alloysO. Rubel,^{1,*} B. Kunert,¹ S. D. Baranovskii,¹ F. Grosse,² K. Volz,¹ and W. Stolz¹¹*Faculty of Physics and Material Sciences Center, Philipps-Universität Marburg, Marburg D-35032, Germany*²*Institut für Physik der Humboldt-Universität zu Berlin, Newtonstrasse 15, Berlin D-12489, Germany*

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The nearest-neighbor bond configuration affects decisively many important characteristics of semiconductor metastable alloys, in particular the width of the band gap. We study effects of formation of a short-range order in (GaIn)(NP)/GaP heterostructures. Annealing experiments on (GaIn)(NP)/GaP quantum wells reveal a blueshift of the photoluminescence spectra and an enhancement of the photoluminescence quantum efficiency as compared to the as-grown material. We show that the replacement of Ga-N bonds by In-N bonds upon annealing can account for the observed phenomena, in particular for the enhancement of the band gap. Calculations carried out in the frame of the density-functional theory and also using an empirical energy functional show that the driving force for the rearrangement in the nitrogen local environment is reduction of the strain contribution to the alloy total energy functional. Analytical treatment of correlation effects on the configurational entropy contribution to the alloy free energy is suggested. We show that the entropy factor is not negligible and it plays a crucial role when determining the thermodynamically favorable atomic configuration.

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I. INTRODUCTION

It is often assumed that physical properties of semiconductor alloys are solely determined by their chemical composition. However, complex semiconductor alloys possess rather different electronic properties at fixed chemical composition depending on the nearest-neighbor bond configuration.¹ For instance, the width of the band gap is very sensitive to the bond configuration. This issue is of high practical importance for metastable semiconductor compounds, in particular for diluted nitride alloys that evidence structural changes after annealing at high temperatures.²⁻⁷

Recently, a new class of dilute nitride semiconductors—quaternary (GaIn)(NP) alloys—has become a subject of intensive investigations with respect to their structural and optical properties.⁸⁻¹⁷ Successful fabrication of light-emitting diodes with a (GaIn)(NP) active layer has been demonstrated.⁸ (GaIn)(NP) alloys are also considered as suitable materials for emitter/collector of heterojunction bipolar transistors.⁹

Our work was stimulated by annealing experiments in (GaIn)(NP)/GaAs quantum wells (QWs) with very high indium content^{9,11,14} that show a blueshift of the photoluminescence (PL) spectra and an enhancement of the PL quantum efficiency as compared to the as-grown material. Here we study such effects on (GaIn)(NP)/GaP QWs with much lower indium content and observe similar trends. Such annealing effects are also typically observed in (GaIn)(NAs) alloys¹⁸ and they are attributed to annealing-induced enhancement of the number of In-N bonds as compared to the as-grown structures.^{1-7,19} However, it is not straightforward to extend this argument to (GaIn)(NP) alloys.

As shown by Kim and Zunger¹ for (GaIn)(NAs) alloys, reduction of the strain energy due to formation of In-N bonds does not imply that In-N complexes should necessarily form. In terms of the alloy cohesive energy, Ga-N bonds are preferred in contrast to In-N bonds. The thermodynamically fa-

vorable state is determined by minimization of the energy functional that contains both chemical and strain energies¹ as well as the entropy factor and, therefore, requires quantitative analysis of particular bond configurations.⁵ Moreover, even if one proves In-N bonds as energetically more favorable than Ga-N ones in bulk (GaIn)(NP), the exchange from the gallium-rich to indium-rich nitrogen local environment does not obviously result in an enhancement of the band gap. Here we examine theoretically a possibility for exchange of Ga-N to In-N bonds upon annealing and the impact of such a rearrangement on the optical band gap in (GaIn)(NP) alloys.

Our theoretical consideration is carried out in the framework of the approach suggested by Kim and Zunger.¹ We use the valence force field (VFF) model in order to determine a strain contribution to the alloy formation enthalpy. It was convincingly shown by Kent and Zunger²⁰ that the VFF model enables one to reproduce the structural relaxation in the neighborhood of isolated nitrogen impurities in GaP and in GaAs. In order to verify the accuracy of strain energies obtained with the VFF model in GaP, we perform here a series of density-functional theory (DFT) calculations for various In-N substitutional configurations. In order to complete the thermodynamic consideration, we calculate analytically the configurational entropy contribution to the alloy free energy at final temperature. It is shown that the exchange from Ga-N to In-N bonds, which might be stimulated by the annealing process, is indeed energetically favorable in GaP based dilute nitride semiconductors. Finally, using the DFT we demonstrate that such a rearrangement should lead to the increase of the band gap. Hence the formation of In-N bonds is a possible mechanism that accounts for the blueshift of PL peak energy observed in (GaIn)(NP)/GaP QWs upon annealing.

II. EXPERIMENTAL DETAILS

All (GaIn)(NP)/GaP multi-QWs used for this study have been grown on (001)-oriented GaP substrates in a commer-

cial horizontal reactor system (Aix-200-GFR) by metal organic vapor phase epitaxy (MOVPE) using hydrogen carrier gas at low reactor pressure of 50 mbar. Due to the metastability of (GaIn)(NP), low temperature MOVPE growth conditions at 525 °C using the efficiently decomposing group-V-sources tertiarybutyl phosphine (TBP) and 1,1-dimethylhydrazine (UDMHy) in combination with the group-III-sources triethyl gallium (TEGa) and trimethyl indium (TMIn) have been applied. The studied heterostructures consist of 15 nm thick (GaIn)(NP) QWs separated by 36 nm thick GaP barriers. The postgrowth annealing step for 1 h at temperature 750 °C has been carried out in the MOVPE reactor under TBP stabilization.

The PL measurements have been performed at temperature 7 K using a continuous wave Ar⁺-ion laser at the emission wavelength of 514 nm. The PL signal was dispersed by a 1 m grating monochromator (THR 1000 from Jobin-Yvon) and collected by a GaAs-detector applying the standard lock-in technique.

The nominal indium and nitrogen composition were determined by high-resolution x-ray diffraction combining measurements of (GaIn)(NP)/GaP structures with those of (GaIn)P/GaP reference samples and assuming that the incorporation of indium is not affected by the presence of nitrogen.

III. MODELING

A. Valence force-field model

In order to reveal the effect of the bond rearrangement on the alloy internal energy, we employ the valence force field supercell method used previously by Zunger *et al.* for (GaIn)(NAs) and Ga(NP) alloys.^{1,20} One or more substitutional nitrogen and/or indium atoms are placed in a large periodical supercell and relaxed with respect to the total strain energy. Here we use a supercell containing 2744 atoms, which provide well-converged strain energies with respect to the size of the supercell. The internal energy of the system per atom as a function of its coordinate can be approximated by the energy functional¹

$$E_s = E_{\text{strain}}(\mathbf{r}_s) + \frac{1}{2} \sum_{i=1}^4 E_{\text{chem}_{si}}, \quad (1)$$

where $E_{\text{strain}}(\mathbf{r}_s)$ is the strain energy per atom s and $E_{\text{chem}_{si}}$ is the cohesive energy per bond between atoms labeled s and i . For E_{chem} we use the experimental values of the cohesive energies reported in Ref. 21 for the binary compounds (see Table I), assuming that E_{chem} is independent of the local strain caused by substitute atoms. The summation index in Eq. (1) runs over the nearest-neighbor atomic species.

The strain contribution to the energy functional in Eq. (1) is determined using the valence force-field model in the form given by Keating²² generalized for zinc-blende mixed crystals.²³ According to the model, the elastic strain energy per atom s can be expressed in the form

TABLE I. Force-field parameters (α, β), equilibrium bond length (r_0), and cohesive energies (E_{chem}) for the zinc-blende binary solids.

Compound	α (N/m)	β (N/m)	r_0 (nm)	E_{chem} (eV)
GaP	44.49	10.70	0.2360	-1.78
GaN	81.40	17.10	0.1957	-2.24
InP	39.53	6.60	0.2541	-1.74
InN	66.30	9.60	0.2167	-1.93

$$E_{\text{strain}}(\mathbf{r}_s) = \frac{1}{4} \sum_{i=1}^4 \frac{3}{4r_{0_{si}}^2} \alpha_{si} (\mathbf{r}_{si} \cdot \mathbf{r}_{si} - r_{0_{si}}^2)^2 + \frac{1}{4} \sum_{i=1}^4 \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{3}{4r_{0_{si}} r_{0_{sj}}} \beta_{isj} (\mathbf{r}_{si} \cdot \mathbf{r}_{sj} - r_{0_{si}} r_{0_{sj}} \cos \theta_{0_{isj}})^2, \quad (2)$$

where $s, i,$ and j are the atomic labels, r_0 is the equilibrium interatomic distance, θ_0 is the equilibrium bond angle, $\mathbf{r}_{si} = \mathbf{r}_s - \mathbf{r}_i$ is the relative position vector of atomic species, and α and β are the force constants which are related to the stiffness constants of binary solids.²² In the case of mixed crystals, an additional approximation is required when determining the bond-bending force constant β_{isj} for asymmetrical bonds, i.e., when the chemical species i and j are not identical. The averaging procedure^{24,25} $\beta_{isj} = (\beta_{isi} + \beta_{jsj})/2$ is usually applied in order to resolve this problem. Force-field parameters for the compounds studied here are listed in Table I. The parameters for GaP and InP were determined from experimental values of the stiffness coefficients and lattice constant.²⁶ For the zinc-blende nitrides we use the force-field parameters suggested in Ref. 25. We would like to note that the expression for the elastic strain energy given in Ref. 25 [Eq. (2)] is incorrect. However, all numerical results where obtained there using the correct form of the strain energy as in Eq. (2) of the present paper and, therefore, are applicable here.

B. *Ab initio* total energy calculation

The total energy calculation is carried out using DFT²⁷ and *ab initio* norm-conserving Hamann pseudopotentials.^{28,29} Wave functions are expanded in a plane wave basis set with the cutoff energy 80 Ry. The Brillouin zone of the 64-atom supercell is sampled using $2 \times 2 \times 2$ Monkhorst-Pack \mathbf{k} -point mesh.³⁰ For the exchange-correlation functional we use the generalized-gradient approximation.³¹

Although it was found that the explicit treatment of gallium $3d$ and indium $4d$ electrons as the valence electrons is necessary in order to reproduce structural and elastic properties of zinc-blende $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys,^{25,32,33} such a treatment results in a poor electronic structure of nitrides (see Sec. B2 in Ref. 33 for details). As a compromise it has been suggested to use pseudopotentials with the nonlinear core

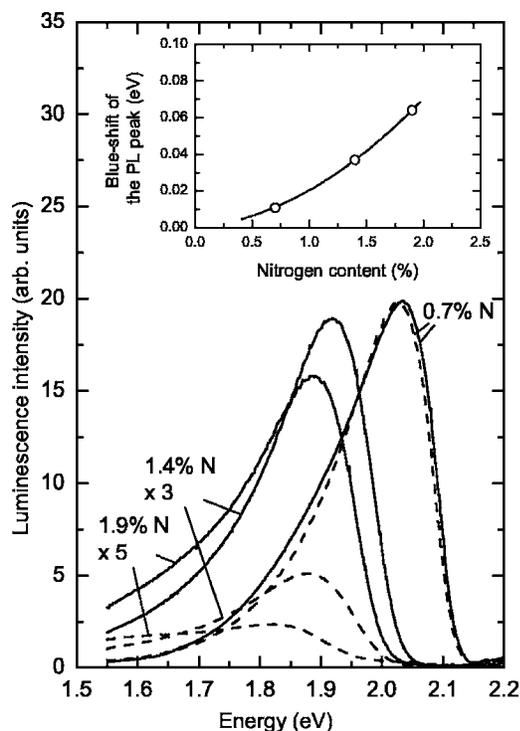


FIG. 1. Photoluminescence spectra of $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_y\text{P}_{1-y}/\text{GaP}$ QWs with the various nitrogen content. Dashed and solid lines are the spectra from as-grown and annealed structures, respectively. The inset represents the blueshift of the PL peak energy after annealing as a function of the nitrogen content; the solid line is a guide to the eye.

correction.³³ Therefore we use here the nonlinear core corrected pseudopotentials for gallium and indium and treat gallium $3d$ and indium $4d$ electrons as core electrons.

IV. RESULTS AND DISCUSSION

A. Annealing-induced blueshift of PL spectra

Photoluminescence spectra taken from the as-grown and annealed $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_y\text{P}_{1-y}/\text{GaP}$ QWs with the various nitrogen content are shown in Fig. 1. The PL spectra exhibit a redshift along with a dramatic decrease of the PL intensity with increasing the nitrogen content (the so-called band gap bowing). The PL linewidth is 0.19 eV for the sample with the lowest nitrogen content and it slightly increases with raising the amount of nitrogen. The PL linewidth is approximately by an order of magnitude larger than that in $(\text{GaIn})(\text{NAs})/\text{GaAs}$ QWs with comparable nitrogen content.³⁴ This indicates the essential effect of disorder on optical transitions, possibly, due to the fact that the localized states related to nitrogen are formed *below* the conduction-band minimum of GaP unlike that in GaAs, where the nitrogen state is located *above* the conduction-band minimum.²⁰

Annealing improves the PL intensity by approximately a factor of 5 in the sample with the highest nitrogen content. The improvement becomes less pronounced with decreasing the nitrogen content. PL spectra of the annealed samples clearly evidence the blueshift as compared to the as-grown

structures. The absolute shift of the PL peak energy after annealing increases with increasing the nitrogen content (see the inset in Fig. 1). Remarkably, the PL linewidth is affected not significantly by the annealing. The experimental features quoted above are in line with the observations on $(\text{GaIn})(\text{NP})/\text{GaAs}$ heterostructures^{9,11,14} and these features resemble the annealing effects inherent to $(\text{GaIn})(\text{NAs})$ alloys.¹⁸

Two alternative mechanisms that account for the blueshift of the PL spectra can be suggested based on the experience with $(\text{GaIn})(\text{NAs})$ alloys. First, redistribution of indium and/or nitrogen atoms with predominant formation of In-N bonds reduces the band gap bowing, i.e., results in an increased band gap.^{1,2} Second, the blueshift of the PL spectra can also be attributed to the smoothing of the disorder potential and hence to elimination of the energetically deep radiative states in the band tails.^{34,35} In the case of $(\text{GaIn})(\text{NAs})$ both mechanisms are relevant, while the former mechanism dominates in the absolute value of the blueshift.

The effect of the change in the characteristic energy of the band tail on the PL peak energy position can be analyzed in the similar way as it is done in Ref. 34. In the following we address the rebonding mechanism as a possible cause of the annealing-induced blueshift of the PL spectra in $(\text{GaIn})(\text{NP})$ alloys. We start with verifying whether there is a driving force for the exchange from Ga-N to In-N bond configurations in $(\text{GaIn})(\text{NP})$ dilute nitrides.

B. Rearrangements in nitrogen local environment

One could expect that the statistics of nitrogen bonds in as-grown $(\text{GaIn})(\text{PN})$ follows the same rule as in $(\text{GaIn})(\text{NAs})$ alloys. Particularly, it is anticipated that the number of Ga-N bonds in as-grown material dominates over a random statistics due to stronger cohesive properties of the Ga-N bond than of the In-N one (see E_{chem} values in Table I), that results in higher affinity of nitrogen to gallium than to indium during the surface reconstruction process. In the bulk, however, the situation can be different, since highly strained Ga-N bonds can relax forming In-N complexes likewise as in $(\text{GaIn})(\text{NAs})$ alloys.^{1,5} The thermodynamically preferable state will be determined by minimizing the alloy free energy, which includes the zero-temperature internal energy E of the system and the contribution of the configurational entropy S at annealing temperature T

$$A = E - TS. \quad (3)$$

Let us first determine the impact of In-N bond formation on the internal energy of the system.

In the following we assume that during annealing indium atoms are fixed on their lattice sites, while nitrogen atoms can move from one group V site to another forming a thermodynamically stable structure. In order to illustrate the interaction of nitrogen with its neighbors, the formation of nitrogen-centered tetrahedra $\text{N}-\text{Ga}_{4-i}\text{In}_i$ with $i=0 \dots 4$ embedded into GaP is considered. Our aim is to evaluate the change in the internal energy caused by formation of such tetrahedra from noninteracting between each other indium and nitrogen atomic species in a large GaP supercell. By the

TABLE II. Strain, chemical, and interaction energies (eV) of various nitrogen and indium substitutional configurations in GaP host supercell.

Local configuration	E_{strain}	ΔE_{strain}	ΔE_{chem}	ΔE
GaP:N	1.25			
GaP:In	0.18			
N-Ga ₃ In ₁	0.95	-0.48	0.27	-0.21
N-Ga ₂ In ₂	0.68	-0.93	0.54	-0.39
N-Ga ₁ In ₃	0.48	-1.31	0.81	-0.50
N-Ga ₀ In ₄	0.35	-1.62	1.08	-0.54

analogy with the energy functional in Eq. (1), the change in the internal energy of the system due to the change in bond configurations of isoelectronic substitutional impurities can be split into strain and chemical components

$$\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{chem}}. \quad (4)$$

The change in the strain energy and in the chemical bond energy of the system caused by formation of N-Ga_{4-i}In_i tetrahedra in the GaP host crystal can be expressed as

$$\begin{aligned} \Delta E_{\text{strain}}(\text{N-Ga}_{4-i}\text{In}_i) &= E_{\text{strain}}(\text{N-Ga}_{4-i}\text{In}_i) - E_{\text{strain}}(\text{GaP:N}) \\ &\quad - iE_{\text{strain}}(\text{GaP:In}), \end{aligned} \quad (5a)$$

$$\Delta E_{\text{chem}}(\text{N-Ga}_{4-i}\text{In}_i) = i(E_{\text{chem}}^{\text{InN}} + E_{\text{chem}}^{\text{GaP}} - E_{\text{chem}}^{\text{InP}} - E_{\text{chem}}^{\text{GaN}}). \quad (5b)$$

Here $E_{\text{strain}} = \sum_s E_{\text{strain}}(\mathbf{r}_s)$ is the strain energy of a relaxed supercell determined using the VFF model; the notation $\underline{\text{A}}\underline{\text{B}}:\text{C}$ denotes that an isolated C-atom is substituted for the underlined B-species. The negative sign of ΔE corresponds to the mutual attraction between impurities, while a positive value ΔE would indicate their mutual repulsion.

Results for the change in the internal energy ΔE due to formation of the N-Ga_{4-i}In_i complexes with $i=1..4$ in GaP are listed in Table II. It is clearly seen that the exchange from Ga-N+In-P to Ga-P+In-N bond configuration (case N-Ga₃In₁) reduces the strain energy by -0.48 eV, while the chemical bond energy increases by 0.27 eV. The resulting interaction energy of such a configuration is negative (-0.21 eV) that indicates the attractive character of In-N bonds in (GaIn)(NP) alloys. The internal energy of the system continuously decreases with increasing the number of indium atoms in N-Ga_{4-i}In_i complexes (see Table II). This tendency persists up to three indium atoms, while adding the fourth indium atom to the tetrahedra does not result in a significant additional energy gain (see Table II). Qualitatively this tendency is similar to (GaIn)(NAs) alloys,⁵ while the energy gain from formation of In-N bonds in (GaIn)(NP) is only about half of that in (GaIn)(NAs) alloys. It is worth mentioning that even the smallest absolute value ΔE in Table II is twice as large as the error bar of the VFF method (see the Appendix).

Now we can utilize the interaction energies obtained for particular In-N bond configurations to characterize the effects of atomic rearrangement on the alloy internal energy.

The problem of finding the thermodynamically stable state of an alloy can be solved by performing elaborated Monte Carlo simulations as it is done for (GaIn)(NAs) in Ref. 1. We would like to emphasize, however, that an analytical solution of this problem is possible, assuming that the strain fields induced by N-Ga_{4-i}In_i complexes do not interact with each other. Let us consider an arbitrary alloy where N-Ga_{4-i}In_i configurations appear with some probabilities p_i which are different from the corresponding probabilities p'_i in the reference alloy (in our case we selected the random alloy as the reference one). Then the change in the alloy internal energy per one substitutional nitrogen atom will be determined by ΔE_i values from Table II, weighted by the differential probability of finding different N-Ga_{4-i}In_i complexes

$$\Delta E_N = \sum_{i=0}^4 (p_i - p'_i) \Delta E_i, \quad (6)$$

where the subscript i refers to the number of indium atoms in the complex. If we assume that the distribution of indium and nitrogen atoms is random, the probability of finding the N-Ga_{4-i}In_i bond configuration follows the binomial distribution

$$p'_i = \frac{4!}{i!(4-i)!} x^i (1-x)^{4-i}, \quad (7)$$

where x is the indium content.

Correlated alloys are characterized by affinity of nitrogen atoms to the lattice sites with indium atoms in the nearest-neighbor shell. Various correlations in atomic distributions are possible. They are described by a different set of probabilities p_i . Here we consider the simplest situation when nitrogen atoms are restricted to randomly occupy only sites with a specific minimum number of indium atoms. For example, we denote as N→In₂₋₄ the alloy, where nitrogen atoms occupy sites with at least two indium atoms as their nearest-neighbors.

Next we need to determine the entropy-related energy change per nitrogen atom due to the In-N ordering in Ga_{1-x}In_xN_yP_{1-y} alloys as a function of its chemical composition and the degree of order. This problem can be solved *exactly* (see the Appendix for details). The change in the configurational entropy per nitrogen atom due to In-N correlation can be expressed as

$$\Delta S_N = y^{-1} k_B [(y-1) \ln(1-y) + (\vartheta-y) \ln(\vartheta-y) - \vartheta \ln(\vartheta)], \quad (8)$$

where y is the nitrogen content and $y < \vartheta < 1$ is the correlation factor which is defined as a fraction of sites in the group V sublattice that are allowed to be occupied by nitrogen. The case $\vartheta=1$ corresponds to the random alloy, i.e., $\Delta S_N=0$. The factor ϑ can be evaluated as a sum of probabilities to find clusters with particular numbers of indium atoms. In the case of N→In_{j-4} the correlation factor has the form

$$\vartheta = \sum_{i=j}^4 p'_i. \quad (9)$$

TABLE III. Changes (eV) in the internal energy ΔE_N , the entropy factor $-T\Delta S_N$, and the free energy ΔA_N of $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.025}\text{P}_{0.975}$ alloy per one nitrogen atom due to rearrangements in its local environment at finite temperature $T=1023$ K.

Alloy	ΔE_N	$-T\Delta S_N$	ΔA_N
As-grown	0.08	0.04	0.12
Random	0	0	0
Correlated:			
$\text{N} \rightarrow \text{In}_{1-4}$	-0.16	0.10	-0.06
$\text{N} \rightarrow \text{In}_{2-4}$	-0.32	0.28	-0.04

We use our model to analyze the thermodynamical stability of the experimentally relevant $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.025}\text{P}_{0.975}$ alloy with various In-N correlations. The ΔE_N energies corresponding to $\text{N} \rightarrow \text{In}_{1-4}$ and $\text{N} \rightarrow \text{In}_{2-4}$ correlations are listed in Table III. The higher order correlations are not shown here, since at this particular chemical composition there are simply not enough In-rich clusters in order to distribute all nitrogen atoms. The alloy internal energy continuously decreases with increasing the In-N correlation. Although the ordering results in the decrease of the internal energy of the alloy, it also diminishes a number of possible microstates and subsequently pulls down the entropy. The entropy factors corresponding to various degrees of order at annealing temperature are listed in Table III. It is clearly seen that the entropy factor is not negligible and it strongly increases with the increasing degree of correlations.

Obtained values for the alloy free energy of correlated structures should be compared with that of the as-grown alloy. In the as-grown (GaIn)(NP) alloy we assume that all nitrogen atoms are coordinated exclusively by gallium atoms for the reasons discussed above. Comparison results for the alloy free energy in Table III for the as-grown and correlated structures yields the energy gain of 0.18 ± 0.08 eV per one nitrogen atom due to breaking of Ga-N and formation of In-N short-range order in the $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_{0.025}\text{P}_{0.975}$ alloy. Therefore one can anticipate increasing of the In-N bonds in (GaIn)(NP) alloys upon annealing.

For the sake of simplicity, we disregarded here the effects of epitaxial strain on the alloy internal energy. Strictly speaking the values of the strain energies in Table II are valid for alloys which are lattice-matched to GaP. Generalization of the model would require the knowledge of the corresponding values of the strain energies as a function of lateral and/or longitudinal strain components which is beyond the scope of the paper.

So far we have shown that a predominance of In-N bonds over Ga-N ones in (GaIn)(NP) alloys can be expected, provided diffusion of nitrogen and/or indium atoms is promoted, e.g., by annealing at a high temperature. In the following section we analyze the impact of such a rearrangement in the nitrogen local environment on the band structure of the (GaIn)(NP) alloy.

C. Effect of the exchange in nitrogen local environment on the band structure

In order to determine the impact of the rearrangement in the nitrogen local environment on the optical band gap in

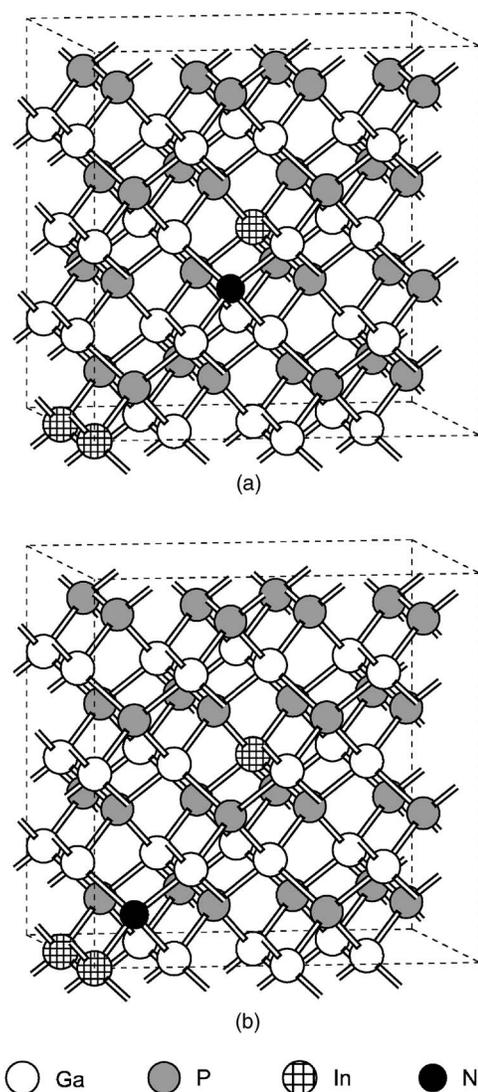


FIG. 2. Geometry of two $\text{Ga}_{29}\text{In}_3\text{N}_1\text{P}_{31}$ periodical supercells with alternative spatial arrangements of substitutional indium and nitrogen atoms: (a) no indium atoms in the first nearest-neighbor shell of nitrogen and (b) one indium atom in the first nearest-neighbor shell of nitrogen.

(GaIn)(NP) alloys, we perform the DFT structural relaxation and subsequent band structure calculation of the two alternative $\text{Ga}_{29}\text{In}_3\text{N}_1\text{P}_{31}$ atomic structures shown in Fig. 2. Although these two structures have the same chemical composition (9% In and 3% N which is in the experimentally relevant compositional range), they differ by the arrangements of substitutional nitrogen atom. The atomic configuration with no In-N bonds [Fig. 2(a)] is attributed to so-called “as-grown” structure. In the “annealed” structure [Fig. 2(b)] one In-N bond is present.

Band structures of “as-grown” and “annealed” atomic configurations are shown in Fig. 3. The Kohn-Sham eigenvalues are calculated for k -points of reciprocal space along the $\Gamma-X-M-R-\Gamma-M$ path in the first Brillouin zone shown in the inset of Fig. 3. Both structures yield a direct band gap $E_g \approx 1.1$ eV, which is, however, less than the energy of the PL emission ($E_{\text{PL}} \approx 1.9$ eV) due to the error in-

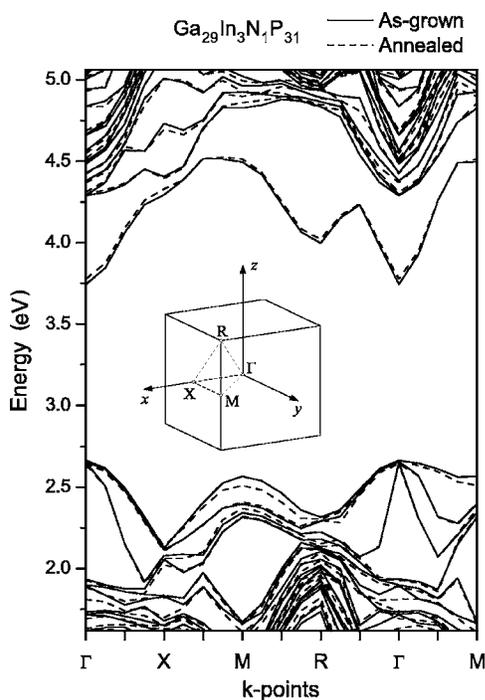


FIG. 3. Band structure of $\text{Ga}_{29}\text{In}_3\text{N}_1\text{P}_{31}$ with various arrangements of nitrogen atom. The solid lines correspond to the case of no indium atoms in the first nearest-neighbor shell of nitrogen [Fig. 2(a)]. The dashed lines correspond to the case of one indium atom in the first nearest-neighbor shell of nitrogen [Fig. 2(b)]. The inset illustrates high symmetry k -points in the first Brillouin zone of the 64-atom supercell.

roduced by the exchange-correlation approximation. The conduction band edge is well-separated from the rest of the band being quite dispersive. These features resemble results of the DFT band structure calculations reported for diluted Ga(NAs) and (GaIn)(NAs) alloys.^{2,36} It is, however, not straightforward to determine the impact of the rearrangement on particular gap energies at k -points relevant for a two-atom basis (Γ, X, L) due to the zone folding. Despite the existing method to classify the alloy states in terms of the high-symmetry states (Γ, X, L),³⁷ we intentionally avoid discussions of these details, since we are interested in the relative change of the band gap between two structures only.

Comparing results on the band structure calculations for the as-grown and annealed structures in Fig. 3, one can conclude that the exchange in nitrogen local environment primarily affects the conduction band, while the valence band edge at Γ -point remains almost unchanged. The data in Fig. 3 clearly evidence the increase of the band gap at Γ -point, which is relevant for the optical transitions, by approximately 30 meV due to formation of the In–N bond in the $\text{Ga}_{29}\text{In}_3\text{N}_1\text{P}_{31}$ supercell. The calculated change of the band gap agrees well with calculations by Klar *et al.*,² which predict increasing of the band gap by approximately 20–40 meV due to the transition from Ga_4 coordination to In_1Ga_3 coordination of a nitrogen atom in (GaIn)(NAs) alloys. The possible interpretation of the widening of the band gap could be a stronger interatomic interaction due to the reduced stretching of nitrogen bonds when forming bonds

with indium.⁴ This result along with the atomic structure calculations in Sec. IV B allows one to conclude the spatial correlation of indium and nitrogen atoms as a possible cause of the blueshift of PL spectra observed in (GaIn)(NP)/GaP QWs upon annealing.

V. CONCLUSIONS

We have studied the effect of the nitrogen nearest-neighbor bond configuration on the optical properties of (GaIn)(NP) alloys. Optical measurements evidence blueshift of the PL spectra in $\text{Ga}_{0.9}\text{In}_{0.1}\text{N}_y\text{P}_{1-y}$ /GaP QWs after annealing. We suggest a theory which shows that the observed blueshift is a consequence of formation of the short-range order in the nitrogen local environment, namely an increase of the number of In–N bonds in (GaIn)(NP) alloys after annealing. This conclusion is supported by the empirical energy functional calculations that predict affinity of In–N bonds due to substantial reduction of the alloy total energy. The analytical treatment of the entropy factor is suggested and it is shown that in the case of a highly ordered alloy this factor plays a decisive role when determining the energetically stable states. First principle calculations of the electronic structure show that the formation of In–N bonds in (GaIn)(NP) alloys leads to the widening of the band gap, which is consistent with the experimental observations.

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APPENDIX

Justification of the VFF accuracy

In order to check the accuracy of the VFF model we compare the strain energies computed using Eq. (2) with those obtained from the DFT calculations, which is done similar in spirit to Ref. 25. For the comparison, we choose a tetragonal GaP supercell, which contains 16 atoms. The strain energy is calculated for several substitutional configurations (GaN_1P_7 , $\text{Ga}_7\text{In}_1\text{P}_7$, and $\text{Ga}_7\text{In}_1\text{N}_1\text{P}_7$) imposing the periodical boundary conditions. When performing these calculations, the positions of the nuclei were relaxed, while the supercell maintains its original size that corresponds to the DFT equilibrium lattice constant of binary GaP.

The strain energy of ternary alloys (e.g., $\text{GaN}_y\text{P}_{1-y}$) is extracted from the total energy calculations using the relation

$$E_{\text{strain}}(y) = E_{\text{tot}}(y) - (1-y)E_{\text{tot}}^{\text{GaP}} - yE_{\text{tot}}^{\text{GaN}}. \quad (\text{A1})$$

Here $E_{\text{tot}}(y)$ is the total energy derived from a supercell DFT calculation for $\text{GaN}_y\text{P}_{1-y}$ with the fraction of nitrogen atoms y ; $E_{\text{tot}}^{\text{GaP}}$ and $E_{\text{tot}}^{\text{GaN}}$ represent the total energies of equivalent supercells containing only bulk GaP or GaN, respectively. In

TABLE IV. Force-field parameters (α, β) and equilibrium bond lengths (r_0) for the zinc-blende binary solids determined from DFT calculations and used exclusively for test purposes.

Compound	α (N/m)	β (N/m)	r_0 (nm)
GaP	40.7	11.1	0.23510
GaN	69.6	15.7	0.19431
InP	28.5	5.95	0.26374
InN	46.0	6.3	0.23395

the case of quaternary alloys (e.g., $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{P}_{1-y}$), the strain energy is defined as

$$E_{\text{strain}}(x, y, b) = E_{\text{tot}}(x, y, b) - (1 - x - y)E_{\text{tot}}^{\text{GaP}} - xE_{\text{tot}}^{\text{InP}} - yE_{\text{tot}}^{\text{GaN}} - b(E_{\text{tot}}^{\text{InN}} + E_{\text{tot}}^{\text{GaP}} - E_{\text{tot}}^{\text{InP}} - E_{\text{tot}}^{\text{GaN}}). \quad (\text{A2})$$

Here b is the fraction of In–N bonds in the total number of bonds in the supercell. The last term in Eq. (A2) subtracts the difference in cohesive energy of the alloy caused by the formation of In–N bonds.

The DFT strain energies should be compared with the results of the VFF calculations for the same atomic arrangements. In order to ensure self-consistency of obtained results, the VFF calculations are performed with the force-field parameters given in Table IV, which were calculated using structural and elastic properties of zinc-blende binaries obtained from the DFT calculations.³⁸ Results for the strain energy caused by different isoelectronic substitutional impurities in a GaP 16-atom supercell are listed in Table V for two methods: DFT and VFF. By comparing DFT and VFF results in Table V one can conclude that the VFF model reproduces the DFT results for the strain energy within the error bar of 0.065 eV.

Thermodynamic consideration

Let us consider a large $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{P}_{1-y}$ supercell containing M atoms. In this supercell the distribution of indium atoms is random, while nitrogen atoms can be distributed randomly as well as with some correlation, characterized by the correlation factor ϑ defined in Eq. (9). Our aim is to find out the change in configurational entropy of the system caused by such a spatial correlation per one nitrogen atom

TABLE V. Comparison between strain energies (eV) caused by substitution of indium and nitrogen atoms in GaP 16-atoms host super cell calculated using different techniques.

Atomic configuration	DFT	VFF ^a
$\text{Ga}_7\text{P}_7\text{N}_1$	1.50	1.59
$\text{Ga}_7\text{In}_1\text{P}$	0.52	0.47
$\text{Ga}_7\text{In}_1\text{P}_7\text{N}_1^{\text{b}}$	1.74	1.72
$\text{Ga}_7\text{In}_1\text{P}_7\text{N}_1^{\text{c}}$	1.19	1.23

^aResults were obtained using the force-field parameters listed in Table IV.

^bNo indium atoms in the nitrogen nearest-neighbor shell.

^cOne indium atom in the nitrogen nearest-neighbor shell.

$$\Delta S_{\text{N}} = 2(S_{\text{ord}} - S_{\text{rnd}})/My. \quad (\text{A3})$$

Here S_{rnd} and S_{ord} are the entropies of mixing for the random and partly ordered systems, respectively. For the entropy we use the definition $S = k_B \ln(\Omega)$, where k_B is the Boltzmann constant and Ω is the number of possible microstates, i.e., the number of possible arrangements of the constituents. In the case of the random alloy the standard approach can be used in order to determine the entropy of mixed crystals. For the quaternary alloy it is the product of possible combinations of atomic configurations in group III and group V sublattices

$$\Omega_{\text{rnd}} = \binom{M/2}{Mx/2} \binom{M/2}{My/2}, \quad (\text{A4})$$

where $\binom{a}{b}$ is a binomial coefficient. The number of microstates in the correlated alloy can be found in the same manner, provided the occupancy of $M\vartheta/2$ available lattice sites by nitrogen-atoms is random. This yields the number of microstates for the ordered structure

$$\Omega_{\text{ord}} = \binom{M/2}{Mx/2} \binom{M\vartheta/2}{My/2}. \quad (\text{A5})$$

Substituting Eqs. (A4) and (A5) into Eq. (A3) one obtains the ΔS_{N} value, which rapidly converges with increasing the size of the supercell M . It can be shown using a Stirling's series that in the limit of an infinitely large supercell the entropy change caused by correlation effects has the exact form

$$\Delta S_{\text{N}} = y^{-1}k_B[(y-1)\ln(1-y) + (\vartheta-y)\ln(\vartheta-y) - \vartheta\ln(\vartheta)]. \quad (\text{A6})$$

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