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Columnar [001]-oriented nitrogen order in Ga(NAs) and (GaIn)(NAs) alloys

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By calculations in the framework of the valence force field method, we show that nitrogen atoms in diluted $GaAs_{1-x}N_x$ tend to align along the [001] direction. In quaternary alloys $Ga_{1-y}In_yAs_{1-x}N_x$ this tendency is observed only in "as-grown" samples, while in the annealed samples nitrogen atoms build more energetically favorable bonds with indium. Experimentally observed inhomogeneous strain profiles in these material systems, as well as their dissolution upon annealing, agree qualitatively with results of the calculations. © *2004 American Institute of Physics*.
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Numerous studies have attempted to identify the arrangement of nitrogen atoms in Ga(NAs) and (GaIn)(NAs) alloys. Scanning tunneling microscopy measurements by McKay *et al.*[1] in diluted Ga(NAs) show the enhanced number of [001]-oriented nitrogen pairs. For quaternary (GaIn)(NAs) alloys, considerable efforts have been focused on determining the changes in the nitrogen local environment upon annealing. Experimental studies show that in "as-grown" (GaIn)(NAs) samples nitrogen is mostly bound to gallium, while in annealed samples In–N bonds dominate.[2–4] Theoretical study of the role of N and In impurity substitutions in GaAs was carried out by Kent and Zunger,[5] and Kim and Zunger.[6] They studied the energetics of various N and In configurations in the lattice by the valence force field (VFF) method and also by density functional calculations corroborating [001]-oriented N–N pairs in Ga(NAs) (Ref. 5) and also, showing changes in local N-bonding from Ga-rich to In-rich environment upon annealing in (GaIn)(NAs) alloys.[6] In previous calculations, the energetics of nitrogen configurations along the [001] direction was considered mostly for N–N pairs.[5] Recent experimental data obtained in Ga(NAs) and (GaIn)(NAs) quantum wells (QWs) by applying a special dark-field transmission electron microscopy (DFTEM) technique revealed [001]-oriented columnar strain fields with a spatial distribution correlated to the nitrogen content.[7]

In this letter, we present results of our calculations for the energetics of nitrogen configurations particularly in the [001] direction taking into account several alternative nitrogen centered N-$Ga_{4-i}In_i$ $(i=1\dots4)$ configurations in GaAs (Fig. 1). In contrast to previous studies,[5,6] we address longer chains of nitrogen atoms and show that their formation in Ga(NAs) is energetically favorable. We also show a way for dissolution of [001]-oriented nitrogen order in (GaIn)(NAs). The theoretically predicted trends are verified by DFTEM experimental data.

In our calculations, we employ the VFF supercell method used previously in Refs. 5 and 6. According to this method, one or more substitutional N or In atoms are placed in a large supercell and relaxed with respect to the total strain energy. We used the supercell of size $5\times5\times8.5$ nm^3 containing 10 456 atoms, showing adequate convergency of the total strain energy. The energy functional depends on atomic positions $\mathbf{R}_i$ and on the chemical composition as

$$E_i = E_{\text{strain}}(\mathbf{R}_i) + \frac{1}{2}\sum_{j=1}^{4} E_{\text{chem}_{ij}}. \quad (1)$$

Here, $E_{\text{chem}_{ij}}$ is the cohesive energy for bonds of type ij. For these energies, we used the experimental values reported for the binary compounds (see Table I).

The strain energy E_{strain} was evaluated in the framework of the Keating VFF model.[8] Bond-stretching and bond-bending coefficients (see Table I) were derived from the elastic constants and from the equilibrium bond lengths of the

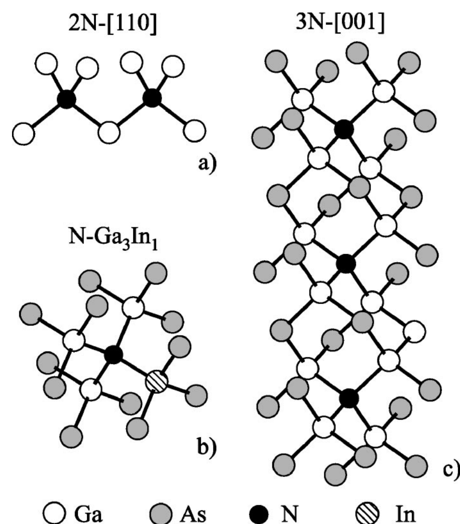

FIG. 1. Geometry of several substitutional impurity clusters in GaAs: (a) N–N nearest neighbor pair, (b) nitrogen-centered cluster with one nearest-neighbor indium atom, and (c) [001]-oriented sequence of nitrogen impurities.

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

Compound	α (N/m)	β (N/m)	r_0 (nm)	E_{chem} (eV)[a]
GaAs	35.46	9.30	0.2448	−1.63
GaN	81.40	17.10	0.1957	−2.24
InAs	33.26	5.76	0.2623	−1.55
InN	66.30	9.60	0.2167	−1.93

[a]Ref. 16.

binary zincblende solids GaAs (Ref. 9), InAs.[10] For GaN and InN compounds, we used the force parameters α and β adopted to elastic parameters calculated for the binary zincblende solids by density functional theory.[11] The bond-bending coefficients, β, of asymmetric bonds (e.g., Ga–N–In) were calculated assuming the additive contributions of both compounds, i.e., $\beta^{(A-B-C)}=1/2[\beta^{(A-B-A)}+\beta^{(C-B-C)}]$.

In order to check a tendency for In and/or N toward clustering in GaAs, we compared the energies of a certain atomic configurations with the energies of infinitely separated In and/or N impurities. For instance, the interaction energy for a $\mathrm{N-Ga_{4-i}In_i}$ cluster is estimated as

$$\Delta E = E(\mathrm{N-Ga_{4-i}In_i}) - E(\mathrm{GaAs{:}N}) - iE(\mathrm{GaAs{:}In}). \quad (2)$$

A positive interaction energy ΔE corresponds to the repulsion between impurities. A negative sign of ΔE would lead to a mutual attraction. In order to verify our results, we first performed calculations for several atomic configurations considered already in previous theoretical studies.[5,12,13] A comparison between our results and those from literature shown in Table II confirms the validity of our calculations. In the following, we present our results for the strain energies of various N configurations first for Ga(NAs) and afterward for (GaIn)(NAs).

For Ga(NAs), the energy gain due to formation of [001]-oriented N-impurity pairs in bulk GaAs has been already shown by Kent and Zunger.[5] We focus here on longer [001]-oriented chains of xN atoms. Our results shown in Table II for 2N-[001], 3N-[001], and 6N-[001] configurations clearly demonstrate that adding an extra N atom to the chain leads to the total energy gain of about 0.2 eV per impurity atom in the chain. This binding energy does not depend on the length of the chain and hence formation of long [001]-oriented N chains is energetically favorable.

TABLE II. Strain, chemical, and interaction energies (eV) of various N and In substitutional configurations in GaAs host crystal.

Local configuration	E_{strain}	ΔE_{strain}	ΔE_{chem}	ΔE
Ga(NAs):				
Isolated N	1.94[a]	…	…	…
2N-[110]	4.38	0.50	0.	0.50[b]
2N-[001]	3.70	−0.18	0.	−0.18[c]
3N-[001]	5.44	−0.38	0.	−0.38
6N-[001]	10.62	−1.02	0.	−1.02
(GaIn)(NAs):				
Isolated In	0.18	…	…	…
$\mathrm{N-Ga_3In_1}$	1.45	−0.67	0.23	−0.44
$\mathrm{N-Ga_2In_2}$	1.02	−1.28	0.46	−0.82
$\mathrm{N-Ga_1In_3}$	0.67	−1.81	0.69	−1.12
$\mathrm{N-Ga_0In_4}$	0.42	−2.24	0.92	−1.32

[a]Previous studies: 1.70 eV (VFF) (Ref. 12); 1.78 eV (*ab initio*) (Ref. 13).
[b]0.38 eV (VFF) (Ref. 5).
[c]−0.1 eV (VFF) (Ref. 5).

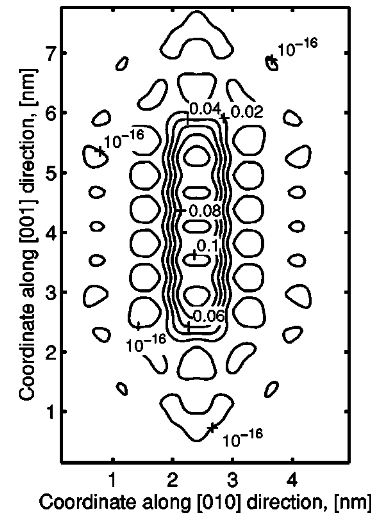

FIG. 2. Strain energy (eV) distribution in the bulk GaAs caused by [001]-oriented chain of five nitrogen atoms.

Figure 2 shows the results of calculations for the (001) plain distribution of strain energy caused by 5N-[001] chain in GaAs. From these data, one can estimate the decay length to be of the order of 1 or 2 nm for the strain fields perpendicular to the chain direction. Recent strain-sensitive DFTEM measurements[7] on the as-grown Ga(NAs) as well as on annealed QWs revealed the [001]-oriented strain fields penetrated through the whole layer of the QW. Moreover, the density of the strain columns increase with increasing N content. Having in mind the above theoretical results, one could attribute the observed strain fields to the thermodynamically stable [001]-oriented N chains in Ga(NAs).

It is worth noting that any N clustering essentially affects the carrier mobility due to more efficient scattering.[14,15] Therefore, in order to improve the carrier mobility, special care should be taken to avoid the formation of the [001]-oriented nitrogen chains.

For (GaIn)(NAs), the nitrogen bonding configuration in as-grown samples is mostly governed by surface processes. Nitrogen on the surface binds preferentially to Ga rather than to In atoms since the cohesive energy for Ga–N bonds is significantly higher than that for In–N ones (see also Table I). However, in the bulk, the binding energy of Ga–N bonds can be lower than that on the surface because of the large strain energy contribution. The calculated data for strain, chemical, and interaction energies in various $\mathrm{N-Ga_{4-i}In_i}$ clusters are given in Table II. It is evident that the strain energy caused by a single N impurity atom drastically decreases with increasing number of In–N bonds. This effect can be explained by a partial compensation of stretching of nitrogen bonds since the equilibrium bond lengths follow the sequence $r_0^{(\mathrm{GaAs})} > r_0^{(\mathrm{InN})} > r_0^{(\mathrm{GaN})}$ (see Table I).

So far, we focused on the strain energy only because in ternary alloys such as Ga(NAs), the chemical energy does not depend on the configuration.[6] Hence, the thermodynamic energy balance in such systems is determined solely by the strain energy. However, in quaternary alloys such as (GaIn)(NAs), the chemical effects are to be taken into

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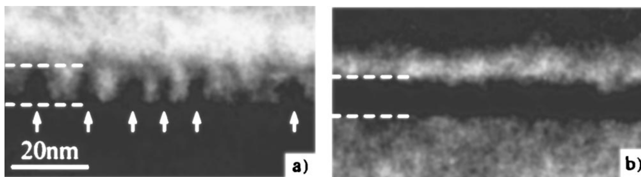

FIG. 3. DF cross-sectional TEM images taken from $Ga_{0.70}In_{0.30}N_{0.027}As_{0.973}$ QWs as-grown (a) and annealed (b). Columnlike strain fields oriented in growth direction within a QW are pointed out by arrows. Dashed lines depict the QW boundaries.

account. The changes in chemical energy, ΔE_{chem}, are listed in Table II for various local configurations. A positive sign of ΔE_{chem} in the Table II indicates a repulsive nature of the chemical contribution to the configurational energy. Since the interaction energy, $\Delta E = \Delta E_{\mathrm{strain}} + \Delta E_{\mathrm{chem}}$, remains negative for any $N-Ga_{4-i}In_i$ configuration listed in Table II, one should conclude that those clusters are thermodynamically stable as was already suggested in Ref. 6. Here, we address the stability of [001]-oriented N chains in (GaIn)(NAs) alloys. It is evident from Table II that the formation of an In–N bond ($\Delta E = -0.44$ eV) is energetically more favorable than the remaining of a nitrogen atom in the chain ($\Delta E \approx -0.2$ eV). Hence, if diffusion of nitrogen is possible, the dissolution of N chains in favor of a more homogeneous distribution of N atoms preferentially bound to In atoms in the bulk (GaIn)(NAs) should occur.

DFTEM images taken from as-grown and annealed (GaIn)(NAs) QWs under strain-sensitive imaging conditions[7] are shown in Fig. 3. The as grown sample—despite a homogenous In distribution—clearly exhibits a columnar strain contrast, which disappears after annealing, in contrast to what is observed for Ga(NAs). The results of our calculations provide a natural explanation for this effect. Diffusion of nitrogen atoms induced by annealing leads to formation of In–N bonds and to dissolving of nitrogen chains responsible for the [001]-oriented columnar strain fields. Further experimental investigation are underway to exactly clarify the length of N chains.

In conclusion, we have shown that in Ga(NAs) the alignment of nitrogen atoms along [001] direction is thermodynamically stable. In (GaIn)(NAs), nitrogen forms more stable In–N bonds, provided this process is supported by diffusion. These results offer a natural explanation of experimentally observed columnar [001]-oriented strain fields in Ga(NAs) and (GaIn)(NAs) as-grown QWs as well as their dissolution in (GaIn)(NAs) upon annealing.

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