Effects of Strain and Local Charge on the Formation of Deep Defects in III-V Ternary Alloys

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The effects of external and internal strains and of defect charges on the formation of gallium vacancies and arsenic antisites in GaAs and $In_{0.5}Ga_{0.5}As$ have been investigated by *ab initio* density functional methods. Present results show that a proper understanding of strain and defect charge permits the development of a *defect engineering* of semiconductors. Specifically, they predict that arsenic antisites in InGaAs ternary alloys can form, upon p-type doping in the presence of an arsenic overpressure, even in the case of high-temperature epitaxial growths.

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The importance of the defect formation energy as a key quantity describing the behavior of defects has been clarified by several theoretical studies investigating the formation of shallow and deep defects in GaAs [1,2] and GaN [3], as well as of shallow defects in ternary InGaAs alloys [4]. Defect formation energies depend on the relative abundances of the atomic constituents (e.g., Ga and As in GaAs) during the crystal growth. If a thermodynamic equilibrium is assumed to hold between the condensed and gaseous phases, these abundances are related to the chemical potentials (μ_{Ga}, μ_{As}) which define the reservoirs from where atoms are taken (or brought) in order to create defects. If the defect is charged, the formation energy also depends on the electron chemical potential, μ_e, which defines the reservoir of electrons [1–5]. In a supercell approach, the formation energy Ω_D of a defect D in GaAs may be written as in Ref. [1]

$$\Omega_D = E_D - n_e\mu_e - n_{\mathrm{Ga}}\mu_{\mathrm{Ga}} - n_{\mathrm{As}}\mu_{\mathrm{As}}\,,$$

where E_D is the energy of a supercell containing n_{Ga} Ga atoms, n_{As} As atoms, and one D defect, and n_e is the number of electrons transferred from an electron reservoir with a chemical potential μ_e to the defect D in a given charge state. It can also be shown that

$$\Omega_D = E'_D - n_e\mu_e - \tfrac{1}{2}(n_{\mathrm{Ga}} - n_{\mathrm{As}})\Delta\mu\,,$$

where the defect energy E'_D is written in the form

$$E'_D = E_D - \tfrac{1}{2}\mu_{\mathrm{GaAs}(B)}(n_{\mathrm{Ga}} + n_{\mathrm{As}}) - \tfrac{1}{2}(n_{\mathrm{Ga}} - n_{\mathrm{As}})(\mu_{\mathrm{Ga}(B)} - \mu_{\mathrm{As}(B)})\,.$$

$\mu_{X(B)}$ is the chemical potential of the X species in the bulk and $\Delta\mu$ is the chemical potential difference $(\mu_{\mathrm{Ga}} - \mu_{\mathrm{As}}) - (\mu_{\mathrm{Ga}(B)} - \mu_{\mathrm{As}(B)})$. In equilibrium, several restrictions apply to the atomic chemical potentials [1]. As an example, in the case of GaAs an excess of As atoms may form a bulk As precipitate. In order to avoid this effect, μ_{As} should not exceed the chemical potential of bulk As, $\mu_{\mathrm{As}(B)}$. Similar considerations lead to the following restrictions to the chemical potentials:

$$0 \le \mu_e \le E_g \quad \text{and} \quad -\Delta H \le \Delta\mu \le \Delta H\,,$$

where E_g is the energy gap and ΔH is the heat of formation of GaAs [1].

These restrictions determine what values of μ_X are relevant to the defect formation. In particular, $\Delta\mu = -\Delta H$ and $\Delta\mu = \Delta H$ correspond to the As-rich limit and the Ga-rich limit case, respectively, i.e., to different growth conditions which may affect the formation of defects. Different values of μ_e are related, instead, to different doping levels, $\mu_e = 0$ corresponding to a Fermi level at the top of the valence band. The above equations for Ω_D are slightly different in the case of InGaAs, where further restrictions apply to the chemical potentials of the cations [4].

Further investigations on the formation of defects in III-V semiconductors have been stimulated by an increasing interest in the *defect engineering* of semiconductors, namely, a controlled introduction of defects aimed to tuning the material properties. As an example, materials for ultrafast optical devices have been obtained by growing GaAs at low temperature (LT) by molecular beam epitaxy (MBE) [6]. This growth leads to nonstoichiometric GaAs, with about 1% excess arsenic, which should favor the formation of As antisites (double deep donors formed by As atoms located at gallium sites) [7] and Ga vacancies. Similarly, arsenic antisites are likely responsible of the ultrafast photoresponses at 1.55 μm achieved in the case of LT-grown InGaAs/InAlAs quantum wells [8]. These experimental works suggest that the introduction of deep defects can improve the optical properties of ternary alloys of interest for optoelectronic devices.

In the present Letter, the theoretical approach introduced in Ref. [1] has been used to perform a careful analysis of the effects of *internal* and *external strain* on the formation of vacancies and antisites in GaAs and $In_{0.5}Ga_{0.5}As$, a ternary alloy that almost matches InP and is of interest for optoelectronic devices [9]. In particular, the combined effect of *strain* and *local charges* on the defect has been

investigated, since it is well known that deep defects are sensitive to lattice and local-charge rearrangements [10]. The results achieved in the case of GaAs have been compared with those found in the case of $In_{0.5}Ga_{0.5}As$ by taking into account that, generally, a ternary alloy (like $In_xGa_{1-x}As$) may be assumed to be given by a binary compound where a fraction x of the cations have been substituted randomly with cations of a different species. This substitution has several effects: (i) the crystal symmetry becomes lower; (ii) the lattice constant (a_0) changes (it increases when the new cation in the ternary alloy is bigger in size than that of the original binary compound); and (iii) the presence of two cations of different size induces an *internal strain*, which is an intrinsic property of the alloy. This strain is mainly accommodated by deformations of the bond angles, while the bond distances, e.g., the Ga-As and In-As distances, are almost equal to those reported in GaAs and InAs, respectively [11]. Present results clarify well the different effects of an internal strain, an external strain, and local charges on the defect on the formation of vacancies and antisites in GaAs and $In_{0.5}Ga_{0.5}As$ and show that these effects permit the development of a defect engineering of these semiconductors. They can also be extended to other pairs of binary/ternary compounds.

The defect energy E_D and the total energies related to the $\mu_{X(B)}$ potentials have been calculated in the local density approximation [12] by using supercells, separable *ab initio* pseudopotentials [13], plane-wave basis sets, the special-points technique for **k**-space integration [14], and the exchange-correlation functional of Ceperley and Alder [15]. The geometry of a given supercell has been fully relaxed by minimizing the forces on the atoms [16]. Convergence tests have been done by using plane-wave cutoffs ranging from 12 to 20 Ry, supercells of 32 and 64 atoms, and **k**-point meshes equivalent to a $(4, 4, 4)$ or $(8, 8, 8)$ Monkhorst-Pack mesh in the zinc-blende unit cell. The results presented here have been achieved by using 64-atom supercells, the $(4, 4, 4)$ **k**-point Monkhorst-Pack mesh in the zinc-blende unit cell, and cutoffs of 18 Ry. The structure of the $In_{0.5}Ga_{0.5}As$ alloy has been simulated by randomly populating the cationic sites of a 64-atom supercell with In and Ga atoms in the stoichiometric ratio. The position of the defect levels in the energy gap has been estimated by calculating the corresponding occupancy levels, i.e., the Fermi-energy values $\epsilon^{n/n+1}$ for which the occupation number of the electronic state changes from n to $n + 1$ [17]. Further details about the calculation procedures can be found elsewhere [18].

Although different types of vacancies and antisites have been investigated, only the results relative to gallium vacancies, V_{Ga}, and arsenic antisites, As_{Ga}, are reported here [19]. These defects have been chosen for their peculiar properties and technological interest. The two defects are complementary: (i) Ga vacancies are deep acceptors and As antisites are deep donors; (ii) vacancies induce local voids in the lattice which lead to a displacement of the nearest neighboring (NN) As atoms *toward* the vacancy [20], while the antisites are characterized by displacements of the NN atoms *far from* the antisite [21]. These displacements are induced by the antibonding interactions of the As_{Ga} with its NN As atoms. Furthermore, both gallium vacancies and As antisites are favored by the presence of an excess of As atoms (a growth condition which favors the realization of materials with ultrafast optical response) [6,7]. Finally, V_{Ga} and As_{Ga} form both in $In_{0.5}Ga_{0.5}As$ and in GaAs, which allows us to compare the defect formation energies in materials *with and without* internal strain, respectively. Then, the formation energies of the As_{Ga}^{0}, As_{Ga}^{+2}, V_{Ga}^{0}, and V_{Ga}^{-3} defects have been estimated in GaAs and $In_{0.5}Ga_{0.5}As$. Since two competing effects are related to the increase of a_0 and to the insurgence of an internal strain on going from GaAs to $In_{0.5}Ga_{0.5}As$, these effects have been investigated separately by introducing two model materials, "strained" GaAs, with a_0 extended to that of $In_{0.5}Ga_{0.5}As$ (GaAs-ext), and strained $In_{0.5}Ga_{0.5}As$, with a_0 contracted to that of bulk GaAs ($In_{0.5}Ga_{0.5}As$-ctd). These model materials provide also a first, qualitative estimate of the effects of an external strain on the formation of vacancies and antisites, although they do not fully reproduce the structure of strained, pseudomorphic heterostructures grown by MBE [11].

Table I gives the formation energies of vacancies and antisites corresponding to the most favorable growth conditions for these defects, $\Delta\mu = -\Delta H$ (i.e., As-rich limit), where ΔH is the heat of formation of GaAs or $In_{0.5}Ga_{0.5}As$ [22]. The position of the Fermi level, which determines the

TABLE I. Defect formation energies of arsenic antisites (As_{Ga}) and gallium vacancies (V_{Ga}) corresponding to the most favorable growth conditions for these defects, i.e., As-rich limit ($\Delta\mu = -\Delta H$, where ΔH is the heat of formation of GaAs or $In_{0.5}Ga_{0.5}As$. GaAs-ext ($In_{0.5}Ga_{0.5}As$-ctd) indicates a model, "strained" material with the lattice constant extended (contracted) to that of $In_{0.5}Ga_{0.5}As$ (GaAs). The last column gives the value of the electronic chemical potential μ_e in the material where the defect forms. The zero of μ_e is taken at the top of the valence band. E_g is the energy gap. All values are given in eV.

Defect	GaAs	GaAs-ext	$In_{0.5}Ga_{0.5}As$	$In_{0.5}Ga_{0.5}As$-ctd	μ_e
As_{Ga}^{0}	0.77	0.26	0.58	0.90	$E_g/2$
As_{Ga}^{+2}	0.07	−0.15	0.11	0.30	0
V_{Ga}^{0}	2.77	2.87	2.74	1.09	0
V_{Ga}^{-3}	1.48	1.80	1.95	0.23	$E_g/2$

charge state of the defects, is reported in the last column of the table. The occupancy levels estimated for As_{Ga} and V_{Ga} indicate that the As_{Ga}^{+2} and V_{Ga}^{0} are stable charge states when $\mu_e = 0$ (Fermi level at the top of the valence band). When the Fermi level is at midgap ($\mu_e = E_g/2$), the stable states are, instead, As_{Ga}^{0} and V_{Ga}^{-3}. In the case of As_{Ga}^{0}, the formation energy of this defect decreases appreciably on going from GaAs to GaAs-ext; see Table I. This behavior can be related to *changes of the local geometry* of the defect; see Table II. In GaAs, the antibonding interaction of the As antisite with its NN As atoms leads to an As_{Ga}-As bond length (2.56 Å) larger than both the calculated Ga-As distance (2.41 Å) and the As-As distance estimated by atomic covalent radii (2.45 Å) [23]. In GaAs-ext, the increase of a_0 (from 5.56 to 5.76 Å) and the corresponding increase of the Ga-As distance up to 2.50 Å allow the As_{Ga}-As distance to relax to 2.63 Å. This relaxation stabilizes the defect and shows that a decrease of the As_{Ga} formation energy is related to an increase of a_0. While the above results agree with the expected behavior of the As_{Ga} defect, a quite surprising picture emerges from the results achieved in the case of $In_{0.5}Ga_{0.5}As$. In this material a_0 also increases with respect to that of GaAs. Moreover, the As_{Ga} loses its tetrahedral symmetry (due to local lattice distortions), which introduces further degrees of freedom for the structural relaxation around the defect. However, these two conditions have not the expected effects on the formation energy of As_{Ga} in $In_{0.5}Ga_{0.5}As$ which is larger than that found for GaAs-ext although the two materials have a same a_0. The increase of a_0 on going from GaAs to $In_{0.5}Ga_{0.5}As$ is compensated, indeed, by the insurgence of an internal strain which leads to As_{Ga}-As distances almost equal, on the average, to those found in GaAs (see Table II). This compensation effect of the internal strain on the As_{Ga} formation energy is confirmed by a comparison of the GaAs and $In_{0.5}Ga_{0.5}As$-ctd cases. Although these materials have the same a_0, the As_{Ga}-As distances in the alloy are shorter (on the average) than those found in GaAs. Accordingly, the formation energy of the defect is larger in $In_{0.5}Ga_{0.5}As$-ctd. In the case of $In_{0.5}Ga_{0.5}As$, the increase of a_0 and the presence of an internal strain have therefore *opposite effects* on the local geometry and the formation energy of the defect. The above results also imply that the formation of As antisites may be favored by an external tensile strain both in $In_{0.5}Ga_{0.5}As$ and GaAs. The charged antisite, As_{Ga}^{+2}, has a different behavior with respect to the neutral defect because: (i) the electronic state responsible for the As_{Ga}-As antibonding interactions corresponds to a defect level in the energy gap; (ii) this level is empty. In GaAs, the latter condition determines a strong reduction of the As_{Ga}-As antibonding interactions which leads to a dramatic reduction of the As_{Ga}^{+2} formation energy. Accordingly, the As_{Ga}-As distances are very close to the As-As bond length estimated by the As covalent radius; see Table II. As a further consequence, the formation energy of As_{Ga}^{+2} is only slightly affected by an increase of a_0, as shown by the close values of Ω_D found for GaAs and GaAs-ext (see Table II). Interestingly, similar results have been found in the case of $In_{0.5}Ga_{0.5}As$, where the closeness of the As_{Ga}-As distances to those found in GaAs and the corresponding small difference in the formation energy values show that the internal strain has minor effects when the As antisite is positively charged. This result is also confirmed by the small increase of Ω_D in the case of $In_{0.5}Ga_{0.5}As$-ctd. It can be concluded that p-type doping has a *major effect* on the formation of As antisites. These defects may also be favored, to a lesser extent, by the presence of an external tensile strain.

In the case of V_{Ga}^{0}, the formation energy of this defect is almost the same in the different materials investigated here but for the case of $In_{0.5}Ga_{0.5}As$-ctd; see Table I. This result can be accounted for by the absence of an internal reconstruction involving the vacancy dangling bonds [20]. This is shown by a comparison of the As-As distances between the As atoms neighboring the vacancy (which are second nearest neighbors) with the As-As distance given by the covalent radii (2.45 Å); see Table II. A weak interaction between the As neighbors of the vacancy implies a smaller sensitivity of this defect to changes of a_0 with respect to the antisites. In $In_{0.5}Ga_{0.5}As$-ctd, the internal strain and the contracted a_0 favor a bonding interaction between two of the four As atoms carrying dangling bonds in the vacancy, as shown by the As-As distance of 2.63 Å found for these two atoms; see Table II. That bonding interaction stabilizes the defect and accounts for the small formation energy. Similar trends are shown by the Ω_D values

TABLE II. The As_{Ga}-As distances between an As antisite (As_{Ga}) and its nearest neighboring (NN) As atoms are reported in the table together with the As-As distances between the NN atoms of a gallium vacancy. In the case of $In_{0.5}Ga_{0.5}As$, the four As_{Ga}-As distances and the three most representative As-As distances between the As neighbors of a vacancy are given in parentheses. GaAs-ext ($In_{0.5}Ga_{0.5}As$-ctd) indicates a model, "strained" material with the lattice constant extended (contracted) to that of $In_{0.5}Ga_{0.5}As$ (GaAs). All values are given in angstroms.

Defect	GaAs	GaAs-ext	$In_{0.5}Ga_{0.5}As$	$In_{0.5}Ga_{0.5}As$-ctd
As_{Ga}^{0}	2.56	2.63	(2.50, 2.55, 2.56, 2.64)	(2.41, 2.46, 2.47, 2.57)
As_{Ga}^{+2}	2.46	2.53	(2.43, 2.46, 2.46, 2.49)	(2.35, 2.38, 2.38, 2.39)
V_{Ga}^{0}	3.75	4.31	(3.30, 3.50, 3.80)	(2.63, 3.10, 3.40)
V_{Ga}^{-3}	3.52	3.89	(3.40, 3.67, 3.78)	(3.00, 3.10, 3.40)

calculated for the V_{Ga}^{-3} defect. However, these values are always smaller than those calculated for V_{Ga}^{0}, thus suggesting the existence of weak bonding interactions between the arsenic atoms neighboring the charged vacancy. This interaction may also account for the small Ω_D value found for the V_{Ga}^{-3} in $In_{0.5}Ga_{0.5}As$-ctd. In general, the formation energies of vacancies result to be significantly larger than those of antisites and slightly affected by strain.

The results achieved in the cases of GaAs and $In_{0.5}Ga_{0.5}As$ may be extended to other pairs of binary/ternary compounds if one takes into account some general properties of antisites and vacancies in III-V semiconductors. Theoretical studies of As_{Ga} in GaAs [21] and P_{In} in InP [24] show that even the latter defect gives rise to antibonding interactions with its NN atoms. This seems a common feature of the antisite defects at the cationic sites, which may be explained by simple chemical arguments: an As_{Ga} antisite uses three electrons to bind to its neighbors, as the substituted cation does. The remaining two (valence) electrons give rise to an excited level in the energy gap and to an antibonding electronic state which makes the formation of antisites sensitive to both an extension and a contraction of a_0. Changes of a_0 may be caused by an external strain or by the presence of cations of different sizes in a ternary alloy. In the latter case, the presence of an internal strain can balance the change of a_0. When the defect loses the "antibonding electrons" the effects of strain are minimized and the antisites have small formation energies both in binary and ternary compounds. In the case of vacancies, generally the vacancies at the cationic sites do not give rise to an internal reconstruction, as it has been found in the case of V_{Ga} in GaAs [20] and V_{In} in InP [24]. This implies a smaller sensitivity of these centers to changes of a_0 and to the presence of an internal strain.

In conclusion, present results show that the formation of vacancies and antisites is related to a *fine interplay* between changes of a_0, internal strain, and charges on the defect. Strain and doping can effectively control the formation of antisites in binary and ternary compounds. It seems difficult, instead, to control the formation of vacancies in the same materials because small formation energies may be achieved for these defects only in the presence of a quite large decrease of a_0. These results have immediate applications in the *defect engineering* of semiconductors. As an example, in the case of $In_xGa_{1-x}As/In_xAl_{1-x}As$ quantum wells LT-grown upon Be doping [8], present results strongly support the formation of As antisites. Furthermore, if thermodynamic equilibrium is assumed, present results *predict* that As antisites can be formed in InGaAs upon p-type doping in an As overpressure even in a *high temperature* growth. This result is of interest for the realization of InP-based structures. In that case, the growth processes require a cracking of molecular species which cannot be achieved in LT processes. As a matter of fact, $In_xGa_{1-x}As/InP$ heterostructures showing ultrafast optical properties have been grown by chemical beam epitaxy at high temperature under high fluxes of arsine [25].

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[1] S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[2] J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993).
[3] J. Neugebauer and C. G. Van de Walle, Festkoerperprobleme **35**, 25 (1996).
[4] Sun-Ghil Lee and K. J. Chang, Phys. Rev. B **53**, 9784 (1996).
[5] Guo-Xin Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **38**, 7649 (1988).
[6] S. D. Benjamin, H. S. Loka, A. Othonos, and P. W. E. Smith, Appl. Phys. Lett. **68**, 2544 (1996).
[7] M. Kaminska and E. R. Weber, *Semiconductors and Semimetals* (Academic, New York, 1993), Vol. 38, pp. 59–89.
[8] R. Takahashi, Y. Kawamura, T. Kagawa, and H. Iwamura, Appl. Phys. Lett. **65**, 1790 (1994).
[9] *Heterojunction Band Discontinuities: Physics and Device Application*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987).
[10] G. B. Bachelet, in *Crystalline Semiconducting Materials and Devices*, edited by P. N. Butcher, N. M. March, and M. P. Tosi (Plenum, New York, 1986), p. 243.
[11] A. Amore Bonapasta and G. Scavia, Phys. Rev. B **50**, 2671 (1994).
[12] R. M. Martin, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter,* edited by J. T. Devreese and P. Van Camp (Plenum, New York, 1985).
[13] R. Stumpf, X. Gonze, and M. Scheffler, Fritz-Haber-Institut, Berlin, FRG Research Report, 1990.
[14] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976).
[15] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[16] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937); R. P. Feynman, Phys. Rev. **56**, 340 (1939).
[17] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980).
[18] A. Amore Bonapasta, Phys. Rev. B **58**, 10 378 (1998).
[19] An extended study on native deep defects in $In_xGa_{1-x}As$ will be published elsewhere.
[20] A. Amore Bonapasta and M. Capizzi, Phys. Rev. B **52**, 11 044 (1995).
[21] A. Amore Bonapasta, Phys. Rev. B **51**, 4172 (1995).
[22] In the case of $In_xGa_{1-x}As$, a further condition has been applied to the potentials of the cations in agreement with their stoichiometric ratio: $\Delta\mu_c = 0$, where $\Delta\mu_c = (\mu_{In} - \mu_{Ga}) - (\mu_{In(B)} - \mu_{Ga(B)})$.
[23] The value of the As atomic covalent radius is 1.225 Å. See J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 22.
[24] A. P. Seitsonen, R. Virkkunen, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **49**, 5253 (1994).
[25] D. Campi (private communication).