Journal of Physics: Conference Series **242** (2010) 012014 doi:10.1088/1742-6596/242/1/012014

Controlling dopant solubility in semiconductor alloys

A. Höglund,[1] C.W.M Castleton,[2] O. Eriksson[1] and S. Mirbt[1]

[1]Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

[1]School of Science and Technology, Nottingham Trent University, Nottingham, NG11 8NS, UK

E-mail: Christopher.Castleton@ntu.ac.uk

Abstract. We consider the formation energies and stabilities of dopants in semiconductor alloys. We show that they are not bounded by the formation energies in the related pure materials. On the contrary, by tuning the alloy composition, dopant solubility can be increased significantly above that in the pure materials. Furthermore, it is not always necessary to carry out full defect calculations in alloy supercells, since good estimates of the formation energies at the most stable substitution sites can be obtained by calculating the formation energies in the various component *pure* materials, but *strained* to the lattice parameter of the alloy.

1. Introduction

Atomic scale point defects play a defining role in a great many industrially and environmentally relevant materials properties and processes, from electronic doping in semiconductors, to hydrogen transport within fuel cells, to the active sites in metal/metal oxide catalysts. Our ability to study such defect properties and processes from as many angles as possible is therefore extremely important. One very important angle is now the use of *ab initio* Density Functional Theory (DFT). [1] The key property usually calculated is the defect formation energy,

$$E_q^F = E_{def}^{Tot}(q) - E_{ideal}^{Tot} - \sum_i n_i\mu_i + q(\varepsilon_F + \varepsilon_V), \quad (1)$$

where $E_{def}^{Tot}(q)$ and E_{ideal}^{Tot} are the total energies of a particular supercell or atomic cluster with and without the charge q defect. n_i atoms of type i and chemical potential μ_i are added while forming the defect. ε_F is the Fermi level, and ε_V is the valence band edge (VBE) measured relative to it. Almost all defect properties can be obtained from E_q^F, and the ways in which it varies with structure, lattice site, host composition, pressure, etc.

The calculation of E_q^F in the bulk of pure materials has become routine (see review [3]) although there remain problems due to the approximations required (see discussion in [4]). Calculations become more complex and expensive if we consider defects at surfaces (e.g. [5]) or interfaces between pure materials (rarely treated [3]), but overall a broad understanding of defects in pure materials has been achieved. However, many of the most important semiconductor materials are not pure at all, but alloys: either binary (e.g. $Si_{1-x}C_{1-x}$), tertiary (e.g. $Al_xGa_{1-x}As$), or quarternary (e.g. $In_xGa_{1-x}As_yP_{1-y}$). Calculations here are far more challenging. The simplest approach is to use the Virtual Crystal Approximation (VCA) [6], in which we replace, say, both the Al and Ga in $Al_xGa_{1-x}As$ with a pseudo-atom whose properties are a weighted average of those of As and Ga. The underlying assumption is that

the properties of the alloy are a linear, or near linear interpolation between the properties of the pure materials, and local details do not matter. For the lattice parameter this is a rather good approximation, known as Vegard's Law [2]: the lattice constant a_0^{AB} of an alloy A_xB_{1-x} is given by $a_0^{AB} = xa_0^A + (1-x)a_0^B$. For some materials the VBE and conduction band edge (CBE) and hence the band gap also follow a similar relation, although more generally there is some curvature. The VCA would predict that in alloys the defect formation energies, E_q^F, vary monotonically, (probably linearly) between those of the pure materials.

However, in most cases [3] the details of local relaxations and the identity of nearby ions make a significant contribution to E_q^F. In a random alloy such as $Ga_xIn_{1-x}P$ some local environments will resemble InP and some GaP, with others in between. One might therefore anticipate a spread of E_q^F values, bounded by those in pure InP and GaP. However, in a recent study of dopants in both alloys and thin multilayers [7] we found that while there *is* a wide spread of E_q^F values, it is *not* bounded by those in the pure materials. Indeed, dopants can be far more stable in the alloy or multilayer than in either pure material, causing significant increases in solubility. Here, we report further results and details regarding the behaviour of dopants in disordered and ordered alloys. Since strain effects turn out to dominate, we consider the examples of Zn_{III}^- and Cd_{III}^- in $Ga_xIn_{1-x}P$. The cationic radii follow the order Zn ≈ Ga < In ≈ Cd, so we can study the substitution of both In and Ga with smaller, similar and larger radius dopants.

2. Computational details

We use plane wave *ab initio* DFT [1] within the Local Density Approximation (LDA) [10] together with ultrasoft pseudopotentials [11, 12] using the VASP code.[13] The indium $4d$ electrons are treated as core, and for charged defects a uniform compensating background maintains the charge neutrality of the supercell.[14]. All ions are relaxed fully. Where both ions and volume are relaxed this is done iteratively, alternating between relaxing the volume with fixed ions and relaxing the ions at fixed volume, until both are simultaneously converged. LDA lattice constants of 5.39 Å and 5.83 Å are used for GaP and InP [8, 9].

Calculations in strained pure materials use 216 atom cells. For the ordered phase of $Ga_{0.5}In_{0.5}P$ we use a 512 atom CuPt structured supercell, [15, 16] with alternating Ga and In atomic layers in the [111] direction. For disordered $Ga_{0.5}In_{0.5}P$ we use 216 atom supercells. (Pair correlations are not optimized, but would have little impact, since the strongest effect turns out to be internal strain - see section 3.) K-point integration is at the $\vec{k} = \frac{1}{4}(1,1,1)$ special point, and the planewave cutoff is 250eV.

Since the two examples defects are both p-type dopants, and we consider the strong doping regime, we assume that the Fermi level lies at the VBE, hence $\varepsilon_F = 0$. For the chemical potentials we use stoichiometric values. If we define $\mu_i = \mu_i^{Bulk} + \Delta\mu_i$, then these correspond to $\Delta\mu_i^{stoich} = \frac{1}{2}\Delta H^{form}$ for $Ga_xIn_{1-x}P$. Here, ΔH^{form} is the formation enthalpy of the compound, such that $\Delta H_{AB}^{form} = \mu_{A_xB_{1-x}} - x\mu_A^{Bulk} - (1-x)\mu_B^{Bulk}$ and the denominator of the prefactor is 2 in this alloy. The bulk chemical potentials are μ_{Ga}^{Bulk}=-3.610 eV, μ_{In}^{Bulk}=-3.269 eV, μ_P^{Bulk}=-6.028 eV, μ_{Zn}^{Bulk}=-1.891 eV and μ_{Cd}^{Bulk}= -1.531 eV. This gives formation enthalpies of -0.59 eV in CuPt-ordered $Ga_{0.5}In_{0.5}P$, -0.62 eV for disordered $Ga_{0.5}In_{0.5}P$.

3. Results

For undoped disordered $Ga_{0.5}In_{0.5}$, full relaxations of both ions and volume gives a_0=5.606 Å. The CuPt-ordered structure has a symmetry axis [111], so without dopants the Ga-P bonding distances are 2.32 Å parallel to [111] and 2.40 Å perpendicular to it, with the corresponding In-P bonding distances being 2.52 Å and 2.47 Å. The resulting average lattice parameter is a_0=5.614 Å. These a_0 values (5.606 Å and 5.614 Å) differ by only +0.07% and -0.05% from the prediction of Vegard's law, which is 5.61 Å using the LDA values for a_0^{InP} and a_0^{GaP}. On the

other hand, the LDA VBE of $In_xGa_{1-x}P$ is not quite so linear. It lies 0.456 eV higher in pure GaP than in pure InP. A linear interpolation therefore predicts a value for $In_{0.5}Ga_{0.5}P$ which is 0.312 eV higher than in pure InP. The values obtained are 0.341 eV and 0.390 eV for the ordered and disordered alloys respectively, which differ by 9% and 25%.

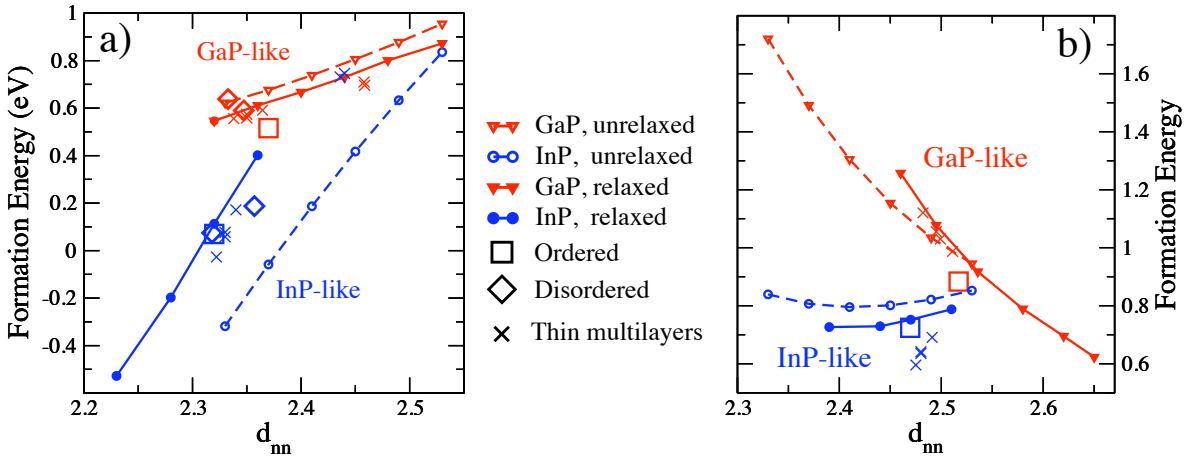

Figure 1. Formation energy of a) Zn^-_{III} and b) Cd^-_{III} in $In_xGa_{1-x}P$, versus average bond length at the dopant site. Lines link values in strained InP or GaP, with (solid) or without (dashed) local relaxation after substitution. (Multilayer data from [7], further details in [17].)

In the ordered alloy, the dopants can occupy two possible sites: in the Ga-planes or in the In-planes. For Zn, E_q^F is 0.45 eV lower when substituting In rather than Ga (see Fig. 1) so the majority of Zn^-_{III} should locate on the In sublattice. Furthermore, E_q^F of Zn^-_{In} is actually 0.35 eV lower than in pure InP, indicating a significant increase in solubility. On the other hand, for Zn^-_{Ga}, E_q^F is practically the same as in pure GaP -just 0.01 eV higher. For cadmium, E_q^F of Cd^-_{In} is close to that in pure InP (0.07 eV lower), but for Cd^-_{Ga} it is 0.38 eV more stable in the ordered alloy than in pure GaP. (In this case the stability improvement of Cd^-_{Ga} will not affect the solubility, as Cd^-_{In} remains 0.16 eV more stable.)

For Zn in the disordered alloy, we consider only sites with either a maximal number of In or of Ga second neighbours, or half of each. As expected, there is a wide spread of E_q^F values, though we only plot the highest two (both with Ga second neighbours) and the lowest two (both with In second neighbours) in Fig 1. We find that the type of second neighbour has rather less influence than the identity of the substituted cation. In practise, only the sites with the lowest formation energies are likely to be occupied, and for these we get very similar results to those in the ordered alloy (a difference of only 0.004 eV). Hence Zn is again considerably more stable than in either pure InP or pure GaP. We have noted elsewhere [7, 17] that we also find a very similar increase in stability in an $(InP)_x/(GaP)_{1-x}$ multilayer structure. (The data are reproduced in Fig 1.) For the multilayers we estimated the resulting defect solubility and its dependence on x. For $x = 0.1$ we found a solubility five orders of magnitude larger than in either pure InP or pure GaP. It seems reasonable to expected a very similar solubility increase if we tune x for either the random or the ordered alloys.

Fig 1 also shows E_q^F for Zn^-_{III} and Cd^-_{III} in pure GaP and InP under strain, plotted both with and without additional ion relaxation after the substitution. Allowing this relaxation lowers E_q^F by an almost constant amount, so the local relaxation energy is more-or-less independent of lattice parameter. Also, when the dopant has a similar size to the host atom substituted (Zn on Ga or Cd on In) there is little local relaxation. If we now compare the relaxed E_q^F in strained pure materials, to those in ordered and disordered alloys and multilayers, we find that they are

very similar. This is significant, since it is computationally much cheaper to calculate E_q^F in the strained pure materials than in either the ordered or disordered alloys, and yet this result gives a reasonable estimate (± 0.1 eV) of E_q^F in the alloy.

4. Discussion and Conclusion

It is clear that the formation energy of dopants in semiconductor alloys depends strongly on the local structure, and in particular on the local strain. It is also clear that there is very little effect, regardless of the identities of second neighbours, when the dopant is of a similar size to the ion substituted (Zn on Ga or Cd on In). Large increases in dopant stability relative to the pure materials occur only when there is a large difference in ionic radii (Zn on In or Cd on Ga.) For example, when $\mathrm{Zn}_{\mathrm{In}}^{-}$ forms in InP, the four Zn-P bonds formed are stretched significantly beyond their equilibrium length, destabilizing the dopant. However, when we alloy with GaP, the lattice parameter is reduced, since Ga is smaller than In. The Zn-P bonds are then allowed to return closer to their preferred lengths, reducing the formation energy and increasing the stability and hence solubility. Similarly, when $\mathrm{Cd}_{\mathrm{Ga}}^{-}$ forms in GaP, the resulting Cd-P bonds are over-compressed. Alloying with InP then increases the lattice parameter, releasing this stress and lowering the formation energy. To summarize this, if we wish to increase the solubility of dopant Z in alloy $\mathrm{A}_x\mathrm{B}_{1-x}$ (where the formation energy is lower in A than in B), the solubility of Z in A can be raised by alloying it with B if either:

1. If Z is smaller than the substituted ion in A and $a_0^B < a_0^A$
2. If Z is larger than the substituted ion in A and $a_0^B > a_0^A$

Since the identity of the substituted ion is important, (rather than that of the second neighbours,) direct experimental studies of this effect would probably depend upon precise preparation methods, with, say, ion implantation being more likely to achieve a solubility increase. Such studies have not been made to our knowledge, but the results of several earlier studies may be attributed to our strain-solubility mechanism (see [7, 17]). For example, $\mathrm{Mg}_{\mathrm{Ga}}$ accumulates at the interface when cubic GaN is grown on a GaAs substrate.[18] Since Mg atoms are larger than the substituted Ga atoms and GaN is stretched near the interface, the formation energy of $\mathrm{Mg}_{\mathrm{Ga}}$ should be lowered near the interface, explaining the accumulation. Similarly, in some InP/InGaAsP lasers, Zn dopants diffuse over time, and build up inside the alloyed active region. [19] Our results suggest that Zn would indeed be on average more stable there, though further work is needed to confirm this.

References

[1] W Kohn and L J Sham 1965 *Phys. Rev.* **140** A1133
[2] L Vegard 1921 *Z. Phys.* **5** 17
[3] E G Seebauer and M C Kratzer 2006 *Mat Sci Eng R* **55** 57
[4] C W M Castleton, A Höglund and S Mirbt 2009 *Modelling Simul. Mater. Sci. Eng.* **17** 084003
[5] A Höglund, C W M Castleton, M Göthelid, B Johansson and S Mirbt 2006 *Phys. Rev. B* **74** 075332
[6] L Nordheim 1931 *Ann. Phys.* **9** 607
[7] A Höglund, O Eriksson, C W M Castleton and S Mirbt 2006 *Phys. Rev. Lett.* **100** 105501
[8] A Höglund, C W M Castleton and S Mirbt 2003 *Phys. Rev. B* **72** 195213
[9] C W M Castleton and S Mirbt 2005 *Phys. Rev. B* **68** 085203
[10] J P Perdew and A. Zunger 1981 *Phys. Rev. B* **23** 5048
[11] D Vanderbilt 1990 *Phys. Rev. B* **41** 7892
[12] G Kresse and J Hafner 1994 *J. Phys.: Cond. Matt.* **6** 8245
[13] G Kresse and J Furthmüller 1996 *Comput. Mater. Sci.* **6** 15
[14] M Leslie and M J Gillian 1985 *J.Phys.C: Solid State Phys* **18** 973
[15] A Gomyo, T Suzuki and S Iijima 1988 *Phys.Rev.Lett.* **60** 2645
[16] M Kondow, H Kakibayashi, T Tanaka and S Minagawa 1989 *Phys. Rev. Lett.* **63** 884
[17] A Höglund, O Eriksson, C W M Castleton and S Mirbt 2006 *In Preparation*
[18] D J As *et al.* 1998 *Appl. Phys.Lett.* **73** 1835
[19] T Kallstenius, J Bäckström, U Smith and B Stolz, 1999 *IEEE J. Lightwave Tech.* **17** 2584