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Theory of Impurity and Defect Induced Instabilities [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1992 **341**, 247-253
doi: 10.1098/rsta.1992.0098

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Theory of impurity and defect induced instabilities

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A brief review of the current status of our work on substitutional and interstitial impurities and native defects in GaAs and of the modelling process used in the calculations is given. The combined empirical tight-binding and *ab initio* pseudopotential approach utilized in these studies allows for efficient testing of a large number of structural possibilities and the identification of the most relevant ones. Applications of the method and new results for EL2, DX, and self-interstitial defect centres in GaAs are discussed.

1. Introduction

It is now well known that simple point defects and impurities in a III–V semiconductor such as GaAs can give rise to structural instabilities that profoundly affect their electronic and optical properties. In many cases the instability is driven by charge exchange, either between defects or between defects and impurities. A primary goal of research in this area is the identification and understanding of the physical properties of all the charge state dependent stable and low energy metastable states of a defect. With few exceptions, this is a sizeable undertaking because it requires the examination and analysis of an extensive set of structures for various charge states. The enormous computational effort required for this purpose has hindered a complete theoretical examination of the structural and electronic properties of the most fundamental point defects in tetrahedral semiconductors.

Reliance on the most advanced theoretical techniques for electronic and structural studies has the advantage of high accuracy and reliability of the results. These methods are generally quite complex, however, and by their very nature limit the number of options that can be tested within a reasonable time, even on the fastest computers currently available. Optimally, one would like to have a modelling approach that is both reliable and efficient. In this way many ideas can be quickly sorted through and the most promising ones retained for further study. In the work described below a combination of simple and usually reliable empirical tight-binding (Chadi 1978, 1979, 1984) and more sophisticated *ab initio* pseudopotential methods (Ihm *et al.* 1979) were used to optimize the search and characterization of native defects and impurities in GaAs.

A three-dimensionally periodic supercell each containing one impurity or point defect was used in all the calculations. It is quite remarkable that unit cells containing as few as 20–30 atoms can be used to decipher the properties of isolated point defects. The tight-binding energy-minimization procedure was generally used in the beginning phase of the calculations to improve an initial 'guess' geometry and for a quick evaluation of the merits of an idea before the start of self-consistent pseudopotential calculations. A tight-binding approach with only nearest-neighbour

Phil. Trans. R. Soc. Lond. A (1992) **341**, 247–253
Printed in Great Britain
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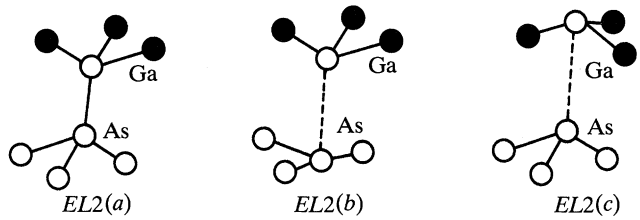

Figure 1. The EL2(a), EL2(b) and EL2(c) configurations for an As-antisite in GaAs are shown. Dashed lines denote broken bonds. The EL2(a) state is the stable state in semi-insulating and p-type GaAs. The EL2(b) state is metastable in semi-insulating GaAs but is the stable state in n-type GaAs. The EL2(c) state is an alternative low energy form of the antisite.

interactions has the great advantage that any reasonable bonding structure, starting with atomic coordinates far from their final equilibrium positions for that particular bonding topology can be examined. As a result, total-energy minima in the configuration coordinate diagram can be found more easily with the tight-binding method than with other methods. The method is also ideally suited for checking the convergence of *ab initio* total energies and atomic relaxations with respect to cell dimensions. This can be done by evaluating the magnitude of residual relaxations and energy changes for larger unit cell sizes, keeping the defect 'core' fixed.

2. The EL2 defect centre

The first defect problem to be examined by this combination of techniques was the As antisite defect in GaAs which results from the placement of an As atom on a Ga site. The defect is known to be at the core of an extensively studied centre labelled EL2 in GaAs (von Bardeleben *et al.* 1986). A most important property of EL2 is its light-induced metastability. The defect can be optically quenched by exposure to *ca.* 1.2 eV sub-band gap light, i.e. the optical absorption is initially strong but it decays with time and cannot be recovered unless the sample is heated to above 100 K in semi-insulating samples. It was originally believed that a simple substitutional defect such as the As-antisite had no low energy metastable states to account for this behaviour and a defect complex consisting of an antisite bound to an interstitial was proposed. An examination of the optical absorption spectrum (Kaminska *et al.* 1985) as a function of uniaxial pressure, however, gave impetus to the idea that EL2 was nothing more than the isolated antisite (labelled as EL2(a) in figure 1). This result, which has received more support recently from photoluminescence measurements (Nissen *et al.* 1991), motivated a search for a possible metastable state of the antisite (Chadi & Chang 1988*a*; Dabrwoski & Scheffler 1988, 1989). The initial search was carried out using the empirical tight-binding method. No metastability was found for small arbitrary displacements of the As antisite from its substitutional site. A low energy state, labelled by EL2(b) in figure 1, was found, however, for a displacement which ruptured an As–As bond. The results of the tight-binding calculations indicated an average charge transfer from the antisite to the other threefold coordinated As atom of about 0.75 e. Without inclusion of coulombic repulsion effects, the energy of the broken bond state was actually found to be *lower* than the fully bonded configuration. The identification of this low energy state of the antisite prompted us to do a full scale *ab initio* pseudopotential calculation which confirmed the large charge transfer and gave a more accurate estimate of 0.25–0.35 eV for the

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energy difference between the stable EL2 (a) and metastable EL2 (b) states (Chadi & Chang 1988a). The results of the calculations for an 18 atom cell were subsequently found to be in very good agreement with detailed studies on a larger 54 atom cell (Kaxiras & Pandey 1989).

More recently we have found a new metastable state of the defect, labelled EL2 (c) in figure 1. Tight-binding and self-consistent pseudopotential calculations indicate that the energies of the EL2 (b) and EL2 (c) configurations are within 0.1 eV $\pm$ 0.1 eV of each other. The EL2 (c) geometry has a lattice-relaxation-sensitive occupied state at 0.09 eV $\pm$ 0.1 eV above the VBM and an unoccupied state only a few hundredths of an electron volt above the conduction band minimum. The small energy difference between the EL2 (b) and EL2 (c) states is indicative of a soft phonon mode at an As antisite. The energy variation in going from the EL2 (b) to the EL2 (c) state is very small with no true minimum at the EL2 (c) configuration.

We have also obtained new results on the properties of As-antisites in n-type GaAs. The stable state of EL2 and of the EL2 (a) configuration of an As antisite in semi-insulating of p-type GaAs have no acceptor levels in the band gap. Each has a deep double donor level which contains two electrons in the neutral state. Despite this, As antisite derived EL2 centres have been identified via electron paramagnetic resonance (EPR) experiments in n-type GaAs (von Bardeleben *et al.* 1987). The experimental data suggest that the number of EPR active EL2 centers in n-type samples is several orders of magnitude large than in p-type or semi-insulating GaAs. The observation of an EPR signal is a strong, but so far neglected, indicator that the stable state of an antisite in n-type GaAs, unlike that in semi-insulating or p-type GaAs, cannot correspond to the EL2 (a) configuration. The results of our calculations lead to the prediction that the stable and metastable states of the antisite become interchanged in going from semi-insulating or p- to n-type GaAs. In the latter case, the negatively charged EL2 $(b)^-$ configuration is 0.12 eV lower in energy than the (EL2 $(a)^0$ + e), where e denotes a free electron in the conduction band and superscripts specify charge states.

The optical depth of the acceptor level of EL2 $(b)^-$ from the conduction band is calculated to be approximately 0.5 eV, about 0.38 eV larger than its thermal ionization energy. My theoretical results also indicate the existence of a *double acceptor* state for the EL2 (b) configuration. This has led Jia *et al.* (1992) to assign the acceptor states of EL2 (b) to the E1 and E2 defects in GaAs. The threefold coordination of the antisite is consistent with their EPR-derived results.

The possibility suggested by an analysis of optically detected electron nuclear double resonance (ENDOR) experiments (Meyer *et al.* 1987) that the stable state of EL2 in semi-insulating GaAs has C_{3v} rotational symmetry consistent with that expected for an antisite-interstitial complex was investigated in detail. A large number of structures were examined but no satisfactory solution consistent with this picture was obtained. The most severe problem with the complex model is its high energy under the constraint of threefold rotational symmetry. The lowest energy configuration of the complex has a split-interstitial structure with no (or at most C_2) symmetry) similar to that proposed by Delerue *et al.* (1987). Imposition of C_{3v} symmetry raises the total energy by nearly 2.5 eV.

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3. Substitutional donors

We have extended the range of our initial investigations (Chadi & Chang 1988*b*, 1989; Zhang & Chadi 1990) on Si and S substitutional donors in GaAs and AlGaAs to Ge, Sn, Se, and Te impurities. It was found that, in each case, the most stable state of the negatively charged DX centre has a structure consistent with that determined previously, i.e. for column IV impurities DX formation involves the motion of the donor atom into a threefold structure (similar to that of the EL2(a) state), whereas for column IV impurities, a displacement of a nearest-neighbour Ga or Al atom into a broken bond 'interstitial' position is required. An alternative mechanism in which DX centres result from a tetrahedrally symmetric 'breathing mode' distortion of the nearest neighbours of a donor was also examined. The negative-U properties of DX centres were found to be preserved for the new state. The energies of the tetrahedrally symmetric DX centres in GaAs are calculated to be within 0.05 eV of those for the threefold symmetric geometries of Sn, Se and Te donors, suggesting that these configurations could occur under suitable pressure or alloying conditions. The tetrahedrally symmetric model is found to be less important for Si and Ge donors.

A third type of negatively charged DX centre was found most recently for Sn donors. In this case the centre arises from the motion of one of the As nearest neighbours of the Sn impurity into an 'interstitial' configuration. This is an analogue of the EL2 configuration for As antisites in GaAs which has nearly the same energy as the 'regular' EL2 state. The new DX structure for Sn is calculated to have an energy within 0.08 eV of the 'traditional' DX centre in which the Sn atom undergoes a large displacement. The three types of DX centres can be distinguished, in principle, by their different optical ionization energies.

4. Interstitial defects

We have recently embarked on an extensive study of the properties of interstitial defects in GaAs and have obtained a number of new and sometimes surprising results. In the initial phase of this work Ga and As self-interstitials in GaAs (and Si interstitials in Si) were studied and a much larger set of structures than in the original pioneering work of Baraff & Schluter (1985) was examined.

An important new result is that Ga and As interstitials have both donor-like and acceptor-like atomic configurations. Arsenic, and gathium interstitials are predicted to self-compensate in undoped GaAs, giving rise to negative-U systems with $U = -0.7$ eV for As and -0.2 eV for Ga. These results are a consequence of the properties of an unusual type of $\langle 110 \rangle$ split-interstitial binding that gives very low energies for several charge states of these defects.

The interstitial binding geometries were determined for four different charge states. The most stable state of a Ga^{+2} interstitial is found for a tetrahedral interstitial site where it is surrounded by four Ga atoms. The four atoms relax outwards by about 0.12 Å†. The other inequivalent tetrahedral site is 0.14 eV higher in energy. The Ga–interstitial bond length to the neighbouring four As atoms is equal to the bulk Ga–As bond length in this case even though there are more distant neighbour relaxations. The tetrahedral geometry for the spin active Ga^{+2} interstitial is consistent with experimental data of Lee *et al.* (1988) for Ga interstitials in GaP.

† 1 Å = 10^{-10} m = 10^{-1} nm.

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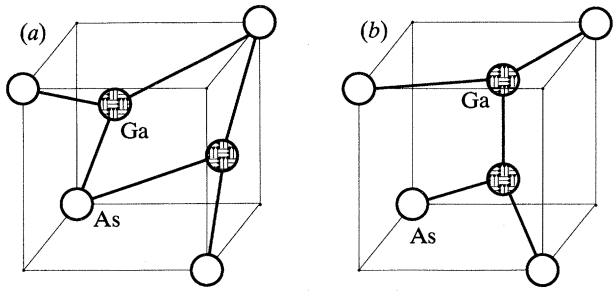

Figure 2. A new ⟨110⟩ split-interstitial geometry for a Ga interstitial defect in GaAs is shown in (*a*) and compared with the usual ⟨100⟩ split configuration in (*b*). The ⟨110⟩ split is unusual in that there is very little bonding between the split interstitials. A ⟨110⟩ split is found to have the lowest energy for several charge states of Ga and As self-interstitials in GaAs.

The singly charged Ga^+ interstitial has a totally different structure. Its lowest energy state occurs for a twofold coordinated configuration in which it breaks a bulk Ga–As bond and forms a bridge bond between the two atoms. This configuration is nearly 1.5 eV lower in energy than for a tetrahedral interstitial one. The neutral and negatively charged states have yet another structure: a ⟨110⟩ split-interstitial configuration shown in figure 2*a*. The bonding is quite distinct from the usual ⟨100⟨ split shown in figure 2*b*. The Ga–Ga distance in the ⟨110⟩ split is 2.7 Å. As a result, the bonding between these atoms is extremely weak and essentially non-existent. The two split-interstitial Ga atoms are threefold coordinated and two of their surrounding four As atoms are fivefold coordinated. It is interesting to note that the ⟨110⟩ split gives an energy within 0.2 eV of the ground state for the *positively* charged twofold coordinated Ga interstitial.

Interchange of the Ga and As labels in figure 2*a* leads to one possible split-interstitial configuration for As. Among eight structures tested, this configuration has the lowest energy for the neutral and negatively charged states of As interstitials in GaAs. It is only for the +2 and +1 charged states of an As interstitial that a ⟨100⟩ like split-interstitial bonding geometry leads to the lowest energy. Charge transfer between the single donor and acceptorlike configurations is predicted to lower the energy of a pair of As interstitials by 0.7 eV. Such a large negative-U value for As interstitials in GaAs may explain why no magnetic resonance identification of any group V interstitial has ever been achieved in a III–V semiconductor, even under high energy electron irradiation conditions (Watkins 1992) where they are known to be produced in large numbers.

The results obtained for self-interstitials in GaAs were extended to Si interstitials in Si. Among all configurations examined, the new ⟨110⟩ split geometry is found to give the lowest energy for positive, neutral, and negatively charged states. For the doubly positive charge state, the ⟨110⟩ split is energetically nearly degenerate with the tetrahedral interstitial configuration. Binding at the hexagonal interstitial site gives a very low energy (about 0.1 eV) metastable state for both the positively charged and neutral states.

The work is now being further extended to B, Be and Al interstitials in Si. Preliminary results for Al indicate that the lowest energies for neutral and positively charged states occur for Al in a tetrahedral interstitial position. The negatively charged state is most stable in a twofold coordinated bridge geometry with the ⟨110⟩ split only slightly higher in energy. Experimentally, the double positive charge state

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of interstitial Al has been identified by EPR (Watkins 1964) and the defect resides in a tetrahedral site. There is also experimental evidence from diffusion studies (Troxell *et al.* 1979) for a substantial rebonding of Al interstitials in p-type Si upon minority carrier injection. This is consistent with our results on the change in bonding configuration when Al becomes negatively charged.

5. Conclusions

A brief review of our latest results on the structural metastabilities exhibited by substitutional and interstitial impurities and native defects in GaAs was given. Low energy metastable structures are found to be a general feature of these systems. Charge exchange either between defects or between defects and impurities plays a significant role in the energetics of defect reactions and has to be taken into account in any complete description of the properties of these centres. Arsenic antisites which are normally double donors in p-type and semi-insulating GaAs are predicted to become double acceptors in n-type GaAs. A new type of split-interstitial bonding that is important in the understanding of the ground state properties of self-interstitials and interstitial impurities in GaAs and Si was obtained. Arsenic interstitials in GaAs are found to be the largest negative-U defects discovered so far in a III–V semiconductor.

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Discussion

A. M. Stoneham (*Harwell Laboratory, Didcot, U.K.*): There is a common belief that semiconductor interstitials have a large entropy. One apparent source of this could be an energy (formation or migration) that decreases rapidly as the cell volume increases with thermal expansion. Have you looked at how your predicted internal energies change with lattice parameter?

D. J. Chadi: The large lattice strains induced by an interstitial make it very likely that the total energy will decrease rapidly with increasing cell volume. I have not yet done any calculations on the lattice parameter dependence of the total energy but plan to do them in the future.

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