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# Nitrogen interstitial defects in GaAs

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## Abstract

We have studied nitrogen interstitial defects in GaAs with first-principles calculations. On the basis of calculated formation energies we have determined the most common nitrogen defects and the transition levels for various charge states. The lowest energy interstitial-type defects are found to be N–N and N–As split interstitials for most of the experimentally relevant conditions. We have also compared two different methods of obtaining the potential correction needed in an accurate calculation of the formation energies and transition levels.

## 1. Introduction

In recent years, dilute nitrogen GaAsN alloys have been a subject of intensive research. Compared to conventional semiconductor alloys, GaAsN presents many unusual properties caused by the large mismatch in size and electronegativity between nitrogen and arsenic atoms. The most important property is the dramatic decrease of the band gap with the introduction of just a few per cent of nitrogen [1, 2].

Previous theoretical work suggests that the majority of N atoms added to GaAs can be expected to go to isoelectronic substitutional As sites [3, 4]. However, the *interstitial* N atoms can still be important defects affecting the electronic and structural properties (such as doping or strain) of the dilute GaAsN alloys. They can be formed in high concentrations, for example, under non-equilibrium conditions during the MBE (molecular beam epitaxy) growth of dilute GaAsN. Several experimental studies have confirmed that most of the nitrogen occupies substitutional As sites but a small fraction can also be found forming various kinds of interstitial defects [5–7]. Most of the theoretical research on N interstitials has concentrated on split interstitials [3, 4, 8]. For a more extensive review of the previous experimental and theoretical research on dilute nitrogen GaAsN, see [1, 9, 10] and the references therein.

Various *neutral* interstitial nitrogen defects in GaAs have previously been studied by some of the authors of this work by using the method of comparing the total energies of supercells with the same composition but different N positions [9]. In the current study we have chosen a general formalism suitable for calculating the formation energies of defects. This formalism allows us to use the chemical potentials to take into account

the growth conditions and also, more importantly, to consider different *charge states* [11]. In addition we have used a larger supercell of 216 atoms which decreases the interaction of the nitrogen defects in neighbouring periodic supercells (decreasing the N concentration from 6% to 0.9%).

In this paper we present our results for the formation energies and transition levels of various interstitial-type defects and discuss the possible effects on the properties of the dilute GaAsN.

## 2. Methods

We have determined the formation energies and transition levels of N defects in GaAs from total energy calculations which are based on density-functional theory (DFT). We used the VASP (Vienna *Ab initio* Simulation Package) code with the projector augmented wave (PAW) method [12] and the local spin density approximation (LSDA) [13]. The well-known DFT-L(S)DA underestimation of the band gap affected our calculations by reducing the value of the band gap energy to 0.53 eV from the experimental value of 1.52 eV [14].

We used a 216-atom supercell with a **k**-point set generated according to the  $2 \times 2 \times 2$  Monkhorst–Pack scheme. The cut-off energy was 400 eV and the gallium 3d states were treated as valence states. A neutralizing uniform background was added in the charged defect cases. Because of the large supercell size, no Madelung corrections were applied. For the lattice parameter of GaAs we used  $5.61 \text{ \AA}$  [10]. The ions were relaxed with the upper limit of  $10 \text{ meV \AA}^{-1}$  on the forces. All symmetries in the supercell were broken prior to the relaxation by displacing the N atoms slightly from the ideal places.

We also performed calculations using a 64-atom supercell with a  $2 \times 2 \times 2$   $k$ -point set to test the effects of the supercell size. The 64- and 216-atom supercells gave similar formation energies and transition levels showing good convergence as a function of the supercell size. For example, the differences between the transition level energies were in all cases less than 70 meV.

We have used the following formalism to determine the prevalent types and transition levels of the different N defects studied in this paper. The formation energy can be defined as

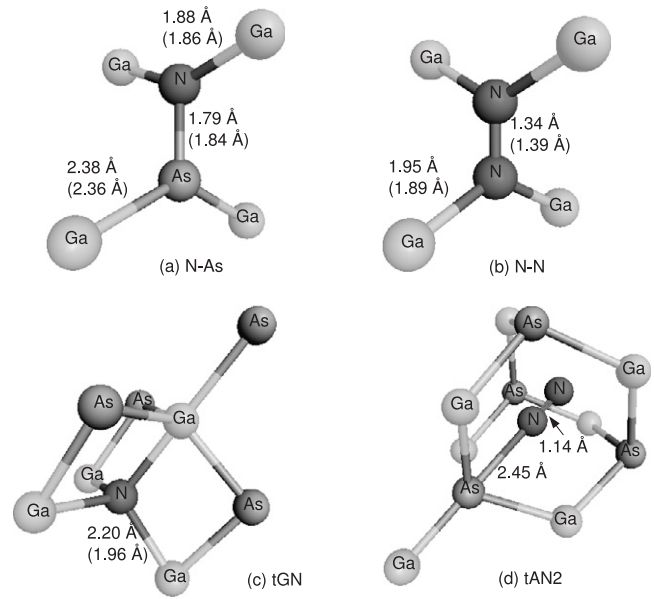
$$E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{GaAs, bulk}] - \sum_i n_i \mu_i + q[E_F + E_v + \Delta V] \quad (1)$$

where  $E_{\text{tot}}[X^q]$  and  $E_{\text{tot}}[\text{GaAs, bulk}]$  are the total energies of the defect X (in charge state  $q$ ) and bulk calculations, respectively. The chemical potentials  $\mu_i$  of  $n_i$  added or removed atoms allow us to take into account the growth conditions. In the next term  $E_F$  is the Fermi energy,  $E_v$  is the valence band maximum (VBM) in the bulk material and  $\Delta V$  is the correction term used to align the potentials in the two supercells. For more details see [10, 11].

We have compared two different methods for determining the potential correction  $\Delta V$ . The potential correction is used to take into account the shift in the potential that results from creating the defect in the supercell due to the use of finite sized supercells and periodic boundary conditions. In the conventional method, used in many previous studies of defects, the value of the potential is estimated in an interstitial region as far from the defect as possible for both the defect supercell and for an equivalent interstitial position in the bulk supercell. We obtain the  $\Delta V$  as the difference of these two values. The second method uses the average electrostatic potential at the core of an ion as calculated by the VASP code. We can calculate the shift in the potential by subtracting the potentials of an atom far from the defect in the defect supercell and a corresponding atom in the bulk supercell. To our knowledge, this method has not been used previously to estimate the potential correction in a defect calculation and in the following we will compare the results given by these two methods (for a similar comparison for band offsets see [15]).

### 3. Results and discussion

In the following we present our results for the formation energies and transition levels of various interstitial nitrogen defects in GaAs. For naming the different cases we use a similar naming convention to [9]. The starting positions before relaxation for single nitrogen atoms were in the centre of a tetrahedron formed by Ga (tGN) or As (tAN) atoms in the zincblende structure or in the middle of the edge of a tetrahedron formed by Ga (eGN) or As (eAN) atoms. We also studied N dimers by placing two N atoms in the middle of a tetrahedron formed by Ga (tGN2) or As (tAN2) atoms. For comparison we have studied the substitutional N on an As site (AN) and a N–N dimer on a substitutional As site (AN2). We have also used the more commonly used names N–As and N–N split interstitial defects for the relaxed eGN and AN2 cases, respectively.

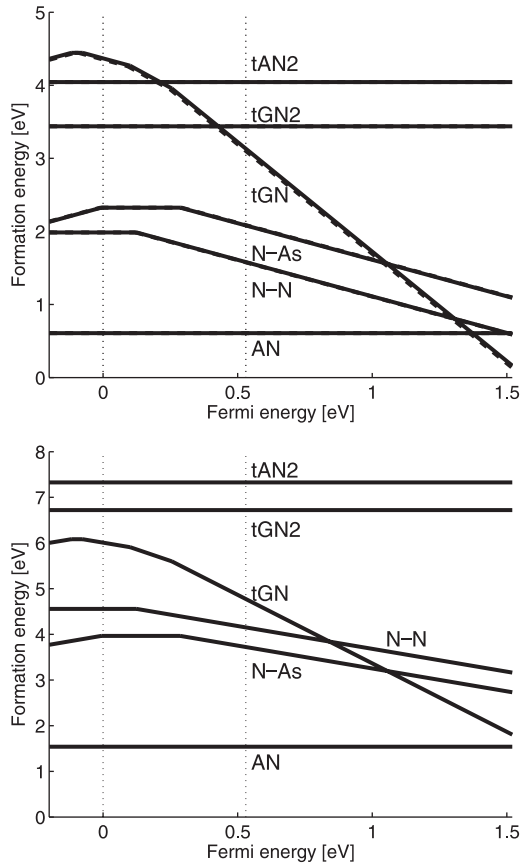


**Figure 1.** The structure of (a) N–As and (b) N–N split interstitial defects and (c) tGN and (d) tAN2 defects in the neutral charge state. Bond lengths shown in brackets correspond to the dominant charge states which are  $-1$  for N–As,  $-1$  for N–N and  $-3$  for tGN.

After the relaxation we found only two stable positions for single interstitial nitrogen: tGN and the N–As split interstitial. The N–As defect is the lowest energy single-N-atom interstitial defect that can be found relaxing the atoms from our starting positions. The final positions for eGN and eAN after the ion relaxation were equivalent to the N–As defect. In comparison, in the previous study [9] the eAN and tAN defects were also found to be stable. In the eAN case this can be attributed to the less tight convergence criterion of the calculations in the previous study. In the current work the tAN defect was found to be metastable in the neutral charge state with a high energy but in other charge states it also became equivalent to the N–As split interstitial after the ion relaxation.

The distances between the interstitial N atoms and closest Ga and As atoms for N–As, N–N, tGN and tAN2 defects are shown in figure 1. In the case of N–As the N atom has moved by  $\sim 0.3$  Å away from the starting position in the middle of the direct line between the Ga atoms towards the closest As atom creating the N–As split interstitial with the bond length of 1.79 Å (slightly smaller than the 1.85 Å in [3]). In the cases of tAN2 and tGN2 the two nitrogen atoms formed nitrogen dimers with the bond length of 1.14 Å which is slightly longer than the experimental bond length of a free  $N_2$  molecule: 1.10 Å. The bond length of a N dimer on the As site (N–N split interstitial or AN2) was found to be 1.34 Å, in good agreement with the 1.35 Å in [4], 1.39 Å in [3] and 1.35 Å in [16].

Next we will discuss the formation energies and transition levels. In the calculation of the formation energy of a defect we need the chemical potentials of the constituents which can be determined in several different ways depending on the assumed growth conditions (for example Zhang *et al* pointed out in [3] that the conditions at the surface during the epitaxial growth can increase the upper limit of the nitrogen chemical



**Figure 2.** The formation energies of various N interstitial defects in GaAs as a function of Fermi energy under As-rich (top) and Ga-rich (bottom) conditions. In the top picture the comparison of the two different methods of calculating the potential correction is also shown. The results obtained using the interstitial regions are shown with solid lines and the core regions with dashed lines. Only those line segments corresponding to the charge state with the lowest energy at each Fermi energy value are shown with the kinks corresponding to the transition levels.

potential). The upper limits to Ga and As chemical potentials (corresponding to Ga- and As-rich conditions, respectively) can be determined from their bulk phases. Using the upper limits, the lower limits can be determined using the equation for the GaAs bulk equilibrium  $\mu_{\text{GaAs}} = \mu_{\text{Ga}} + \mu_{\text{As}}$ . For the nitrogen chemical potential there are two possible choices:  $\mu_{\text{N}_2}/2$  or  $\mu_{\text{GaN}} - \mu_{\text{Ga}}$ . For the As-rich conditions we chose  $\mu_{\text{N}_2}/2$  and for the Ga-rich ones,  $\mu_{\text{GaN}} - \mu_{\text{Ga}}$  (with GaN in the wurtzite structure), which give the lower chemical potentials in each case. Figure 2 shows the formation energies of various N defects as a function of the Fermi energy. In the top graph we have the As-rich conditions and in the bottom graph the Ga-rich conditions.

In the top graph of figure 2 we can see the differences between the formation energies obtained using the interstitial regions or the core regions in the calculation of the potential correction. In most cases the curves coincide and even in the case of tGN the difference is too small to cause even quantitative differences of any significance. On the basis of this, we find the new method of using the average electrostatic potentials at the cores of the ions to be as reliable as the

commonly used method of comparing the potentials of the interstitial regions. In the following analysis the results obtained using the conventional method have been used.

Under almost all conditions studied here we find the lowest energy site for N in GaAs to be the substitutional As site (AN), in agreement with previous studies [3, 4]. For most Fermi energy values the *interstitial* defect with the lowest energy is the N–N split interstitial under As-rich conditions and the N–As split interstitial under Ga-rich conditions. We find only one transition level for both defects in the band gap. The transition from neutral to  $-1$  charge state ( $0/-$ ) happens for N–N and N–As defects at Fermi energies 0.12 and 0.29 eV above VBM, respectively. This means that the neutral charge state is relevant only for p-type material and in most cases the defects are in the  $-1$  charge state. Also the tGN defect can have a formation energy near (or even lower than) the split interstitial defect one if the material is n-type (especially if the growth happens under Ga-rich conditions). It has transition levels ( $-/-2$ ) and ( $-2/-3$ ) at 0.10 eV and 0.26 eV, respectively, above the VBM in the band gap, leaving it in the charge state  $-3$  for most of the Fermi energy values.

In a previous study the N–N split interstitial was found to have a  $(+ / 0)$  transition at 0.2 eV and a  $(0 / -)$  transition at 0.3 eV above the VBM [4]. We do not find a  $(+ / 0)$  transition in the band gap and also the  $(0 / -)$  transition is found closer to the VBM. Possible reasons for this difference are the differences in our computational methods. We included the Ga 3d states as valence states, which causes the VBM to be pushed up [11]. Furthermore, we performed calculations with spin polarization whereas it is not clear whether this was done in [4]. In the earlier study of the different interstitial N cases [9], tGN2 and tAN2 were found to have an energy comparable with the N–As split interstitial (the N–N split interstitial was not considered), which differs from the results of the current study. The most probable reasons can be found in the differences in our methods which are discussed in section 1. The N on As site and N–N split interstitial defects were considered in the neutral charge state in [8] for a range of different chemical potentials. Our results for these defects are in good agreement with their results for the As- and Ga-rich limits. The ordering of our transition levels for the N–N and N–As split interstitial defects agrees with the ordering of the single-particle energy levels of the same defects in [3].

When comparing defects with different amounts of N one should be extra careful, especially in the case of the As-rich conditions, since it is not very clear what the value of the chemical potential of N truly is in the experiments as it can be heavily affected by the growth conditions. For example, having a lower N chemical potential (closer to the value used in the Ga-rich case) would increase the formation energies of all of the N defects, but even more so for the ones with two N atoms (N–N, tGN2 and tAN2), bringing the final picture close to the Ga-rich conditions. Only the N–N defect is affected by the chemical potential of the As which would lift it even higher above the N–As defect. In practice the situation may well be somewhere between these different cases which leads us to the conclusion that we can expect to find in dilute nitrogen GaAsN alloys both the N–N and N–As split interstitials with the actual

order decided by the prevailing experimental conditions. The tGN defect can be expected to be relevant only in n-type materials.

#### 4. Conclusions

In order to obtain a unified picture of the nitrogen interstitial defects in GaAs we have performed formation energy calculations for all of the most important interstitial defect types in different charge states by a DFT method. From the defects studied we have found the N–N and N–As split interstitials to be the most likely to be formed under different experimental conditions. Their most important transition levels in the band gap are (0/–) transitions at 0.12 eV and 0.29 eV above the valence band maximum for the N–N and N–As defects, respectively. We have also performed a comparison of two different methods for determining the potential correction in the calculation of the formation energies and find the new method of using the average electrostatic potentials of the cores of the ions as reliable as the conventional method of using the interstitial regions.

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