Simulations of Nitrogen Incorporation into GaAsN Alloys: 
The Role of Lattice Relaxation

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1 Introduction

Highly mismatched alloy (HMAs) have unique properties that when developed can lead to many exciting improvements. HMA’s provide advancement for solar cells by adding a fourth lattice matched alloy GaAsNBi to the existing GaInP, GaAs, and Ge multijunction solar cell. Due to their tunable electron density of states, HMAs have been proposed for high efficiency thermoelectrics. Finally, progressing our understanding and control of novel qubits in HMAs has promise in creating nuclear spin hyperpolarization, which is key to future solid-state quantum computing. Ref [1] has shown that the spin defects in the Ga(In)NAs alloys facilitate strong dynamic nuclear polarization at room temperature through efficient spin-dependent recombination and hyperfine coupling. To refine these defect qubits we must first have a better grasp on the incorporation of the solute atoms. Specifically, learning how Nitrogen incorporates into GaAs alloys can give information on the material properties and helps us control these properties by changing the type of defect incorporated through methods such as Rapid Thermal Annealing.

Using the nuclear reaction between an incident alpha particle and a nitrogen atom in the lattice, we explore the nuclear reaction analysis (NRA) “yields”, which represent the N concentrations, in each of the [111], [110], and [100] “channels” of the GaAsN lattice. The channels occur where you ori-
Figure 2: Projections of the crystal structure, as well as the total simulated NRA yields in the [100], [110], and [111] directions for (a) NSub, (b) (N-N)As, and (c) (N-As)As are presented. (d) Measured total NRA in each channeling direction. Similar yield trends of $Y_{[111]} > Y_{[110]} > Y_{[100]}$ are observed for (c) and (d), suggesting that (N-As)As is the dominant interstitial complex in GaAsN alloys.

Figure 3: Projections of the GaAsN with (N-As)As, (N-N)As, and Nsub defects in the [100], [110], and [111] directions. In Fig. 2. Meanwhile the measured NRA yield trends, shown in Fig. 2(d), reveal $Y_{[111]} > Y_{[110]} > Y_{[100]}$. Based upon a comparison between the measured and computed NRA yield trends, (N-As)As was considered to be the dominant N interstitial complex. This is developed in Ref. [3] and [4].

In addition to the one unit-cell sized Monte Carlo-Molecular Dynamics (MC-MD) simulations of GaAs:N described above, multiple unit cell simulations up to 5x5x5 have been performed for both GaAs:N and GaAsBi:N. In all MC-MD simulations to date, atomic positions used in the structure input files had not been allowed to relax, and therefore, possible non-equilibrium positions of Ga and/or As induced by NAs or BiAs were not taken into account. In particular, at a recent Gordon Conference, the authors of Ref. [5] suggested that the formation of the N-As pair is too energetically costly to be observed in GaAs, and that
instead, these results might be explained by lattice relaxation associated with substitutional N, NAs. Therefore, the purpose of this study is to compute the “relaxed” atomic positions using Density Functional Theory (DFT) calculations. The DFT determinations of the “relaxed” atomic positions are then used as the structure input files for the MC-MD simulations.

For the DFT simulations, the initial structure consists of 2x2x2 unit cells of GaAs in which one arsenic atom is replaced with a nitrogen atom. The system, including both atomic positions and the supercell size/shape, is allowed to relax to its lowest energy configuration. As shown in Fig. 3, the relaxation allows the Ga-N bond length to decrease from 2.33 Å to 2.08 Å, while the lattice parameter increases by a factor of 1.062. We then use both the unrelaxed and relaxed structures as the input atomic positions for the MC-MD simulations. It is interesting to note that a comparison of the unrelaxed and relaxed structures suggests that the Y[110] increases and the Y[111] decreases with lattice relaxation. As mentioned above, Y[111] > Y[110] > Y[100] for the measured NRA yield trend. Since lattice relaxation associated with substitutional N (i.e. NAs) leads to a decrease in Y[111], the presence of NAs in lieu of (N-As)As seems unlikely.

2 Methods

2.1 Density Functional Theory (DFT)

To determine the position of atoms in the lattice, calculations were done using the first-principles framework of density functional theory (DFT). The code was employed with Quantum Espresso in connection with ultrasoft pseudopotentials (USPP) method and the generalized gradient approximation. The optimization of the atomic structure was performed using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. Atoms along with size and shape of the supercell were allowed to relax until the remaining forces were less than 20 meV/Å. [6] Calculation was performed using a 64 atom supercell consisting of 2ax2ax2a 8-atom unit cells of GaAs with one unit cell including an NSub. The kinetic energy cutoff energy for wavefunctions of 50 Ry and charge density cutoff of 200 Ry was used. The k-points were in the Monkhorst-Pack 2x2x2 scheme.

2.2 Monte Carlo - Molecular Dynamics (MCMD) Simulations

To examine and simulate NRA of nitrogen defect in GaAs, a combined Monte Carlo-Molecular Dynamics approach was used, based on Ref. Each simulation begins by assigning a specified number of alpha particles a random starting point on the surface of the input structure with a subsequent trajectory determined by numerical integration of the Moliere potential function, with a resolution of 2A for each step. As the ion passes through, the simulation records the close encounter probability based on its proximity to the atom type of interest and the equation in Fig. 4. Once the ion reaches a cutoff radius, the distance of two times the
\[ P_{ce} \propto \sum_{i=1}^{N} \exp \left( \frac{-|r - r_i|^2}{2\sigma_i^2} \right) \]

Figure 4: Close encounter probability where \( u_1 \) is the root mean square of thermal vibrational amplitude, \( r \) is the position of the ion, and \( r_i \) is the position of the \( i \)th atom of interest in the lattice.

radius of the atom type you specify, 4 Å is this case, it switches into close-encounter mode to record the probability more accurately, includes shorter time steps, and continues in the mode until it passes the cutoff radius.

To get the predicted NRA yields from this simulation we assume that close-encounter probabilities between the about 5 MeV alpha particle and a Nitrogen will produce detectable protons through the \( ^{14}\text{N}(a,p)^{17}\text{O} \) reaction. We assume that the \( (N-N)\text{As} \) interstitial defect is aligned along the \([111]\) direction and \( (N-\text{As})\text{As} \) is aligned along \([010]\). The relaxed position and structure for NSub is found using DFT while previous simulations assumed it took the exact position of a As. To compare the simulated results with experimental, an alpha particle energy is chosen so that the highest amount of \( ^{14}\text{N}(a,p)^{17}\text{O} \) reactions occur experimentally and the close-encounter probability with respect to depth into sample is summed to produce a total yield in the \([100]\), \([110]\), and \([111]\) directions.

3 Results

3.1 DFT

The DFT simulations showed the expected change in bond length between Ga and NSub decreased from 2.33 Å to 2.08 Å. An unexpected result was that the lattice constant increased by a factor of 1.062. This is unintuitive as the lattice constant for GaN in a zinc blende structure is smaller than GaAs. The relaxed structure is shown in Fig. 6. Ref. [6] also noted that in their much larger cell of 4098 atoms the central \( 2\times2\times2 \) GaAs with the defect decreased by 0.24%. Regardless, the purpose of the DFT is to observe how the local change around the defect affects simulations and the expected displacement around NSub was seen.

3.2 MCMD

A number of different input parameters were varied but the final calculations of unrelaxed and relaxed \( 2\times2\times2 \) GaAs with one NSub were done with parameters SimTime:20.0, SimzVelo:146.66, SimPot-Prox2:16.0, Cryx_Trans:1, and PColl_Atom set to the nitrogen atom. For both unrelaxed and relaxed, I ran five simulations each with 500, 1000, and 10000 alpha particles and summed the output to obtain the final output.
When running my version of unrelaxed, I found it varied from the original simulations that did not take relaxation into account, as seen in Fig. 7. These differences could be explained by some of the following changed properties: original simulations have a concentration of 1 N per 3 As, a 1x1x1 unit cell structure with crystal translation parameter set to two whereas new unrelaxed simulations have a concentration of 1 N per 31 As, a 2x2x2 primitive cell structure with crystal translation parameter set to one. The original and new also had a slightly different lattice constant as I used a relaxed pure GaAs 2x2x2 cell as the basis for my unrelaxed NSub. Things tested that showed to not be the cause of the difference in yield trend include: PColl_Atom parameter, changing whether the Unit is one cell or a 2x2x2 structure (although this about double the total yield for each direction), and changing between using repeatable primitive cells vs using a full unit cell. By performing simulations of a 2x2x2 GaAsN cell with 8 Nsub and 1 Nsub using the previously created MATLAB code to randomly place defects, I found that the likely candidate for the yield trend change is Nitrogen concentration, as shown in Fig. 8.

By comparing the unrelaxed to the relaxed, I saw some changes in the yield trend, displayed in Fig. 9. The [110] increased while the [111] direction decreased. Since the experimental data showed that the [111] direction has the highest yield, a decrease in [111] for NSub makes it an even less likely candidate for a prominent defect and the conclusion that (N-As)As is the dominant defect is still valid as it is the only defect type with the same yield trend as data.
Figure 9: Comparison of the simulated un-relaxed (left) and relaxed by DFT (right) 2x2x2 cell of GaAsN with one Nsub.

Figure 10: The relaxed Nsub NRA yield trend further indicates that (N-As)As is the dominant interstitial.

References


