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Simulations of GaN using an environment-dependent empirical tight-binding model

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We have developed an empirical, total-energy tight-binding model for gallium nitride which we have used in molecular-dynamics simulations of the bulk material as well as several native point defects. The Ga-N and N-N interactions are treated using the standard two-center approximation whereas the Ga-Ga interactions contain three-body effects that make these interactions sensitive to the local environment of the Ga atoms, thus making the model more transferrable than a strictly two-center model. The parameters of this model provide a good fit to experimental data and *ab initio* calculations. [S0163-1829(99)06415-2]

I. INTRODUCTION

Gallium nitride is a promising semiconductor material for optoelectronic applications due to its large (3.5 eV) band gap, which currently allows blue light-emitting diode (LED) and laser fabrication,[1] but which, in principle, can be extend into the ultraviolet. Alloying with In and Al allows custom band-gap engineering. In addition to its optoelectronic properties, the material is chemically and physically hard and its electronic properties make it suitable for high-frequency applications.

These promising applications have motivated many experimental and theoretical groups to strive for a more fundamental understanding of this material. Advances in the growth of GaN have been rapid, but even the best samples have high concentrations of defects including such mesoscopic defects as grain boundaries, inclusions (or precipitates), surface features, and undoubtedly many as-yet unidentified microscopic defects. Understanding such defects, their formation, and, ultimately, their control, would be of great value to the GaN research community. For GaN, theoretical studies[2] will play a crucial role in developing such an understanding, as has been demonstrated in other materials such as silicon and more conventional III-V compounds, most notably GaAs.

Native point defects have been studied theoretically using density functional theory[3,4] although there has been no definitive experimental identification of any of these defects. However, the larger defects mentioned above do not easily lend themselves to treatment by rigorous *ab initio* computational methods. We have therefore developed an empirical tight-binding (ETB) model which allows computationally efficient quantum molecular dynamics simulations of GaN and native defects therein. Eventually this method will be applied to the study of large native defects, surfaces, and growth processes. This basic model can be extended to include impurities, such as the acceptor Mg and especially H, through the addition of appropriate interatomic parameters. The purpose of this paper is to describe our model and present our calculations of bulk GaN properties and native point defects in GaN.

II. DETAILS OF THE MODEL

The theoretical framework for the models used in our simulations is fundamentally a Chadi-type empirical tight-binding (ETB) formalism[5] wherein the total potential energy of the system is composed of a ‘‘band-structure’’ energy E_{bs} and a ‘‘correction energy’’ E_{corr}. E_{bs} is the one-electron quantum-mechanical part of the total energy and is simply

$$E_{bs}=\sum_{i}^{occ.} n_i\epsilon_i , \tag{1}$$

where ϵ_i is the energy eigenvalue of the ith energy level and n_i is the corresponding electron occupancy. The correction energy is constructed as a sum of pairwise potentials,

$$E_{corr}=\frac{1}{2}\sum_{ij}^{i\neq j} U(R_{ij}), \tag{2}$$

where R_{ij} is the distance between atoms i and j. The form of these pairwise potentials differs for the various interspecies interactions, and we extend these below to include nonpairwise, i.e., three-body, effects in the case of the Ga-Ga interactions.

The interatomic Hamiltonian matrix elements are calculated using an sp^3 basis set for both the N and the Ga atoms. Although *ab initio* calculations[6,7] have shown that the Ga $3d$ electrons are important for correctly describing the valence-band electronic density of states and the lattice constant of GaN, including these electronic states in an ETB calculation is not as critical. The reason for this is that the correction energy E_{corr} can be adjusted to compensate for the lack of the $3d$ electrons in the total energy.

For the Ga-N interactions, a strictly two-center approximation is used.[8] Thus, the Hamiltonian matrix elements between sp^3 basis orbitals on different sites depend entirely upon the vector displacement between the orbital centers (nuclei). Following Harrison,[9] we use an interatomic distance dependence of the form

$$V_{ll'm}=V^0_{ll'm}\left(\frac{R_0}{R}\right)^2, \tag{3}$$

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TABLE I. The values of our tight-binding parameters for the various interatomic interactions in our model, evaluated at their respective ''reference'' bond lengths. An a superscript indicates that the left atom is an anion and c denotes a cation. Thus, $V^{0a}_{sp\sigma}$ is the hopping parameter for the interaction of an s orbital on a N and a p orbital on a Ga, etc. The reference bond lengths, R_0 are chosen to be 1.95, 2.93, and 1.108 Å for the Ga-N, Ga-Ga, and N-N interactions, respectively.

Hopping parameters			Self-energies		
Ga-N	$V^{0}_{ss\sigma}=$	-2.52	Ga	E_s	-1.25
	$V^{0a}_{sp\sigma}=$	3.59		E_p	6.00
	$V^{0c}_{sp\sigma}=$	2.54	N	E_s	-9.39
	$V^{0}_{pp\sigma}=$	2.95		E_p	0.00
	$V^{0}_{pp\pi}=$	-1.06			
Ga-Ga	$V^{0}_{ss\sigma}=$	-2.07			
	$V^{0}_{sp\sigma}=$	2.00			
	$V^{0}_{pp\sigma}=$	2.90			
	$V^{0}_{pp\pi}=$	-0.91			
N-N	$V^{0}_{pp\pi}=$	-1.52			
	$V^{0}_{sp\sigma}=$	2.01			
	$V^{0}_{pp\sigma}=$	4.36			
	$V^{0}_{pp\pi}=$	-3.00			

where R is the interatomic distance, R_0 is some reference distance (chosen to be the equilibrium bond length for the given interaction), and $V^0_{ll'm}$ is the strength of this matrix element, or ''hopping parameter,'' at the distance R_0. The above distance dependence works well for the Ga-N interactions, which are the major factors effecting the band gap, E_g. With our parameters, this distance dependence provides a band-gap pressure dependence of $dE_g/dP = 3.1$ meV/kbar, which is on the same order as the experimental value[10] of 4.7 meV/kbar and the *ab initio*[11] value of 4.1 meV/kbar. The hopping parameters and atomic-level self energies were fit to the energy bands calculated by Fiorentini, Methfessel, and Scheffler[7] and are given in Table I.

The correction potentials for the Ga-N interactions are pairwise, depending solely upon the distance between the two nuclei. In the case of the Ga-N interactions, the following form, used by Molteni *et al.*[12] for GaAs, was used:

$$U(R_{ij}) = \phi_1 \exp[(R_0 - R_{ij})/\alpha] + \phi_2 \frac{R_0}{R_{ij}}. \tag{4}$$

The adjustable parameters were fit, along with other parameters to be described below, so that the model would produce a zinc-blende lattice constant of 4.49 Å, a rocksalt phase with a lattice constant of 4.17 Å and a total energy per atom in the rocksalt phase that is 0.75 eV above that of the zinc-blende phase. These values are consistent with experiment and *ab initio* calculations.[11,13,14] The parameters we use are $\phi_1 = 1.64$ eV, $\phi_2 = 0.75$ eV, and $\alpha = 0.275$ Å.

In tight-binding (TB) models, one often excludes from consideration interatomic interactions beyond a certain ''cutoff'' interatomic distance. For molecular-dynamics calculations, wherein the positions of the atoms will be changing, it is necessary to truncate these interactions in a smooth manner. We accomplish this by using a multiplicative ''cutoff function'' applied to both the Hamiltonian matrix elements and the correction potentials;

$$f_c(R_{ij}) = \{1 + \exp[(R_c - R_{ij})/s]\}^{-1}, \tag{5}$$

where R_c is the cutoff distance and s is a measure of the sharpness of the cutoff. This function approaches unity for $R_{ij} < R_c$, and zero for $R_{ij} > R_c$. The two parameters are chosen separately for each type of interatomic interaction. For the case of the Ga-N interactions, the values are $R_c = 2.85$ Å and $s = 0.05$ Å. These values permit 1nn Ga-N interactions in bulk GaN, but produce vanishing Ga-N interactions for more distant pairs.

For the N-N interactions, we fit our model to the known properties of the N_2 molecule. Due to the short 1.108 Å bond length of this molecule, the distance dependence of the Hamiltonian matrix elements was chosen to be

$$V_{ll'm} = V^0_{ll'm} \frac{R_0}{R} \exp[(R_0 - R)/R_0], \tag{6}$$

which provides a shorter range interaction than that used for the Ga-N interactions. The tight-binding parameters (see Table I) were fit so as to reproduce as closely as possible the energy levels of the N_2 molecule.[15] Small corrections to these parameters were later made when we considered certain defects. (See Sec. III.) For the correction potential, we used a procedure similar to that due to Wang, Chan, and Ho.[16] The correction potential is defined so that the ETB model will reproduce a known total-energy curve (versus the interatomic distance) for the N_2 molecule:

$$U(R_{ij}) \equiv E_{total}(R_{ij}) - E_{bs}(R_{ij}). \tag{7}$$

In the equation above, $E_{bs}(R_{ij})$ is calculated using the TB parameters already fit to the electronic structure of N_2. $E_{total}(R_{ij})$ is given by Herzberg[17] in the form of a Morse potential which describes the N_2 bond length and vibrational frequency. Thus, our model reproduces, by construction, the correct bond length, 1.108 Å, and vibrational frequency, 2331 cm^{-1} of the nitrogen molecule. The cutoff parameters [see Eq. (5)] are $R_c = 2.85$ Å and $s = 0.25$ Å.

A. Ga-Ga interactions

1. Environment dependence

The second nearest neighbor ($2nn$, Ga-Ga or N-N) separation is 3.18 Å for both the zinc-blende and wurtzite phases. For the N-N interactions, this distance far exceeds the N_2 molecule's equilibrium bond length, and one would therefore expect the N-N interactions to be of little importance to the bulk electronic structure within a TB model. Bulk Ga metal[18] contains Ga-Ga bonds with lengths of 2.4 to 2.7 Å, which implies that the Ga atoms may interact significantly at the GaN $2nn$ distance. This scenario is supported by *ab initio* defect calculations[3,4] which predict significant Ga-Ga interactions in the case of the nitrogen vacancy in GaN, but little interaction between nitrogens in the case of the Ga vacancy. These defect issues will be addressed below, when we consider the native-defect characteristics predicted by our model. For bulk GaN, we are unable to simultaneously fit our ETB model to both bulk moduli and phonon frequencies by using first nearest-neighbor interactions alone; 2nn interactions, especially those between Ga atoms, are essential.

However, we find that if we use a Ga-Ga model which is appropriate for bulk GaN, our defect calculations are incompatible with the predictions of more rigorous density-functional calculations,[3,4] especially for the N vacancy (V_N) and Ga antisite (Ga_N) defects. It is not surprising that this happens for a simple tight-binding model, which cannot accomodate drastic changes in atoms' surroundings. To correct for this shortcoming we have developed a model for the Ga-Ga interactions which is adaptable to the different environments presented by bulk GaN and bulk Ga. In perfect GaN, Ga atoms interact with one another always as second nearest neighbors, with a N atom, a common neighbor of both Ga atoms, intervening. In bulk Ga, and in many GaN defect situations, the Ga-Ga interactions are not interrupted by the presence of a N atom. We can distinguish between these two situations mathematically by defining a function η_{ij} which characterizes the interaction between Ga atoms labeled i and j,

$$\eta_{ij} \equiv f_c^{\text{Ga-N}}(R_{ik}) f_c^{\text{Ga-N}}(R_{jk}), \tag{8}$$

where k is the N atom which leads to the largest value of η for the given Ga pair, and $f_c^{\text{Ga-N}}$ is given in Eq. (5) with parameters appropriate to Ga-N. Thus, if a N atom is a common neighbor of two Ga atoms, $\eta_{ij}=1$ and an interaction model appropriate to bulk GaN (model A or M_A) is used for this Ga-Ga pair. If the two Ga atoms in question do not have a common N neighbor, $\eta_{ij}=0$ and an interaction model appropriate to bulk Ga is used (M_B). (We are making the approximation that additional common N neighbors will not further affect a given Ga-Ga interaction.) η_{ij} varies smoothly between these two extremes so that the Ga-Ga model for any pair is essentially a mixture of the two extreme models. Schematically,

$$M = M_A \eta + M_B(1-\eta). \tag{9}$$

The above procedure is applied to both the Hamiltonian hopping matrix elements and the correction potentials and the models are as described below.

The correction potential for Ga-Ga has the form

$$U(R_{ij}) = \phi_3 \frac{R_0}{R_{ij}} \exp[\gamma(R_0 - R_{ij})] + \phi_4 \left(\frac{R_o}{r}\right)^{12}, \tag{10}$$

where the second term produces a repulsion that prevents unphysically short bond lengths from occurring. Model A, appropriate to bulk GaN, has $\phi_3 = 1.834$ eV, $\phi_4 = 0.15$ eV, and $\gamma = 0.49$ Å^{-1}. Model B, appropriate to bulk Ga and many defect environments, has $\phi_3 = 3.53$ eV, $\phi_4 = 0.03$ eV, and $\gamma = 0.7$ Å^{-1}. Model B has an additional term of the form

$$\phi_5(1 - 1/\{\exp[(R_b - R_{ij})/s_b] + 1\}), \tag{11}$$

where $\phi_5 = -3.0$ eV, $R_b = 2.1$ Å, $s_b = 0.10$ Å. This term controls the shape of the repulsive potential at short bond lengths. For both correction potentials, $R_0 = 2.90$ Å. The Ga-Ga matrix elements are calculated as in Eq. (3), and both models use the parameters described in Table I. The models also differ in that for model A the cutoff parameters are $R_c = 2.85$ Å and $s = 0.20$ Å and for model B they are $R_c = 3.8$ Å and $s = 0.05$ Å. Thus, model B provides a longer range and less repulsive Ga-Ga interaction.

In principle, all interatomic interactions should be environment dependent, including our N-N and Ga-N interactions. For the sake of manageability, simplicity, and computational efficiency we have made only the Ga-Ga interactions dependent upon the local environment, as we have found these to be the most crucial for reproducing, with a tight-binding model, the experimental and *ab initio* properties of GaN.

III. RESULTS

The parameters of this model were adjusted to obtain what we believe is an optimum fit to both experimental and theoretical data for bulk GaN and theoretical data regarding native point defects. The simulations of perfect GaN were carried out using 64 atom cubic supercells in the case of the zinc-blende or rocksalt structure and 96 atom rectangular supercells for the wurtzite structure. This wurtzite cell is larger than that used by the *ab initio* groups.[3,4] The defect simulations were carried out in the wurtzite supercells. The Γ point of the supercell Brillouin zone was used for solving the electronic Schrödinger equation. The atoms were moved according to the calculated Hellmann-Feynman forces using the Verlet algorithm. The supercell volume was held fixed at the values mentioned below (which lead to a minimum in the potential energy for the bulk material at a temperature of 0 K). All defect calculations are appropriate to the neutral charge state.

A. Bulk properties

Our model reproduces well the bulk structural and electronic properties of GaN (Table II). Our value of 4.49 Å for the lattice constant of the zinc-blende phase is in good agreement with *ab initio* values and experiment. Our results for the wurtzite phase are $a_0^{\text{wz}} = 3.20$ Å and $c_0^{\text{wz}} = 5.23$ Å, which provides the same first- and second-near-neighbor distances as our zinc-blende phase. (The zinc-blende and wurtzite phases of GaN are found to be very similar energetically by both experiment and theoretical studies and this is true of our model as well.) Our calculations yield a perfect wurtzite structure, with $c/a = \sqrt{8/3} \sim 1.633$ and internal parameter $u = 0.375$, although some theoretical studies[6,19] and experiments[20] show small deviations from the ideal structure. Phonon frequencies are also reproduced well (see Table II) using both molecular dynamics simulations and frozen-phonon calculations.

Experiment shows that when exposed to large hydrostatic pressures, GaN undergoes a phase transition into the rocksalt structure[21] at approximately 50 Gpa. Phase curves from *ab initio* calculations are generally in agreement[11,13,10] with estimates of 30–50 Gpa for P_{trans} and a rocksalt lattice constant $a_0^{RS} = 4.10 - 4.20$ Å. Our model gives $P_{trans} = 42$ GPa and $a_0^{RS} = 4.17$ Å. Concurrent with the phase transition is an observed darkening of the GaN crystals, which can be explained by the closing of the band gap below the visible threshold. Our model gives a rocksalt band gap of 2.2 eV,

TABLE II. Results of our model for selected bulk properties of GaN. All items refer to the zincblende structure unless otherwise indicated (RS=rocksalt and WZ=wurtzite). Except where noted, experimental and *ab initio* results are summarized in Refs. 6 and 29. All phonon modes reported below are zone-center ($k=0$) modes except for the ZB L-point TO mode, which is analogous to the WZ Γ-B_1^2 mode. Phonon data are summarized in (Ref. 30). Our phonon frequency data represent results of molecular dynamics simulations using velocity-velocity correlation functions, and are limited to a resolution of ± 5 cm^{-1}.

Quantity	This model	Experiment	*Ab initio*
a_0 (Å)	4.49	4.50	4.50
B_0 (GPa)	289		179–240
a_0^{RS} (Å)	4.17		4.10–4.25
a_0^{WZ} (Å)	3.20	3.189[a]	3.00–3.21
c_0^{WZ} (Å)	5.23	5.185[a]	4.97–5.21
E_{gap}(ZB) (eV)	3.50	3.5	1.5–2.73[b]
E_{gap}(WZ) (eV)	3.50	3.5	1.63–2.89[b]
E_{gap}(RS) (eV)	2.20	<1.55	0.5–1.0
Optical phonon frequencies (cm^{-1})			
Wurtzite			
A_1	545	531, 533	534, 537
B_1^1	402	silent	330, 335
B_1^2	689	silent	677, 697
E_1	548	558, 560	555, 556
E_2^1	291	144	146, 150
E_2^2	565	568	558, 560
Zinc blende			
(Γ-TO)	544		551–603
(L-TO)	690		

[a] Reference 20.

[b] References 6 and 31. Note that *ab initio* DFT methods usually underestimate the band gap. Higher accuracy can be obtained with computationally intensive GW corrections, but these were not included in all of the defect studies cited in other parts of this paper. See Ref. 3 for a short discussion of these DW corrections as they are applied to defect calculations.

which is much smaller than the WZ-GaN band gap and in qualitative agreement with experiment.

B. Native defects

Because the local atomic environments of native defects are significantly different from those of the perfect GaN crystal, it is crucial that we compare our empirical model with the predictions of more rigorous quantum-mechanical calculations. Indeed, it was such comparisons that led us to introduce the environment-dependent Ga-Ga interactions described in the previous section. We concluded from earlier calculations that a strictly two-center model lacked the transferrability needed to adequately describe the native defects (as compared to the *ab initio* calculations).

For each of the defects descibed below, we began the MD simulations using a perfect wurtzite 96 atom supercell to which the appropriate atoms were added or removed. The minimum energy configuration of the defect was then determined by annealing the supercell at an elevated temperature (usually near 1000 K) for several hundred to a few thousand MD time steps and then slowly cooling (via velocity renormalization) until a potential energy minimum was reached. For each defect, several simulations were performed with slightly different initial conditions so as to minimize the possibility of improperly identifying local minima (metastable geometries) as global minima. Also, absolutely no restrictions were made on the atomic relaxations; all atoms were free to move according to their respective Hellman-Feynman forces and Newton's second law.

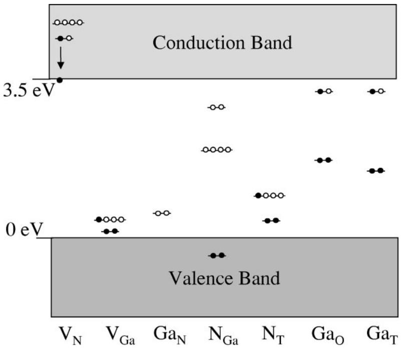

FIG. 1. The electronic structures predicted by our model for the defects discussed in the text. Short horizontal lines indicate electronic levels, with closed circles indicating electronic occupation for the neutral defect. The arrow near the nitrogen vacancy, V_N indicates an electron associated with the defect state is given up to the condution band.

The results of our model agree well with *ab initio* calculations of the Ga and N vacancies in WZ-GaN.[3,4] The N vacancy was long thought to be a likely candidate for a shallow donor that led to the *n*-type conductivity of most as-grown GaN. Although it now appears that impurities such as silicon and oxygen may account for much of this behavior,[22,23] the N vacancy may still be important technologically. We begin our discussion with the N vacancy.

As mentioned earlier, the N vacancy is characterized by a strong interaction among the adjacent Ga atoms. This is concurrent with the hybridization of the dangling Ga bonds. The defect states are primarily an a_1 state resonant in the valence band and a set of three closely spaced levels resonant within the conduction band (in the higher symmetry of the zincblende structure, these three states would form a t_2 triplet). The lowest of these CB resonant states contains one electron that is given up to the minimum CB level (E_c). The electronic structures obtained from our calculations are summarized in Fig. 1. The Ga atoms surrounding the vacancy relax symmetrically outward by about 0.23 Å, and the energy gain for this relaxation is 1.1 eV. Perhaps because we do not take the crystal-field contributions into account explicitly, we do not observe the slight asymmetry in the final defect geometry seen in the *ab initio* studies.

Electronically, we find that the Ga vacancy is primarily a set of weakly interacting N dangling bonds that provide three localized states very near the valence-band maximum (E_v). Because these three twofold degenerate states are occupied by only three electrons they can serve as traps for both electrons and holes, as pointed out by Bogusławski, Briggs, and Bernholc,[3] who obtained a similar geometry and electronic structure. Our model leads to a 0.05 Å relaxation of the N atoms away from the vacancy, which is slightly larger than

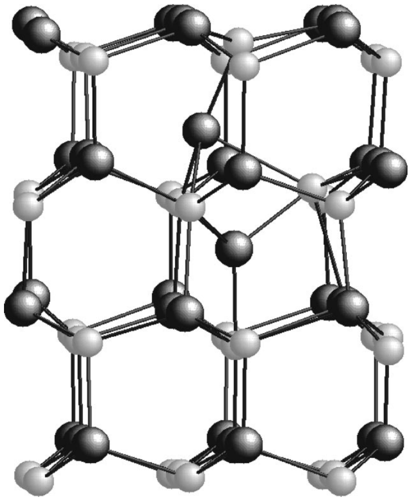

FIG. 2. The Ga interstitial at the *T* site does not move far from the ideal *T* site but it forces a neighboring Ga atom, which was initially directly above it along the *c* axis, into an interstitial region. In this and subsequent figures, the large, dark spheres represent the gallium atoms and the small, lighter spheres are nitrogen atoms.

the 0.01 to 0.05 Å calculated by Neugebauer, and Van de Walle for the neutral charge state.[4] We find that this relaxation lowers the energy by 1.41 eV, which is about twice as large as that calculated by the same group.[24] Although we make this comparison, it should be pointed out that the energy difference between the relaxed and ''unrelaxed'' geometries of a particular defect is not a very meaningful quantity. It cannot be measured experimentally, and it represents only two rather extreme points in a multidimensional potential energy surface.

The Ga interstitial and, especially, the Ga antisite involve a great deal of relaxation. In the case of the antisite, we find that the *c*-axis neighbor moves 0.4 Å parallel to the *c*-axis and away from the central Ga. The other three neighbors move outward so that the resultant Ga-Ga distances are 2.310 Å along the *c* axis and 2.06 Å for the other three. This final geometry is C_{3v} about the *c* axis. The only state in the gap associated with this defect is unoccupied, at $E_v+0.4$, and it is largely a $pp\sigma$ combination of orbitals on the central atom and its *c*-axis neighbor.

Bogusławski, Briggs, and Bernholc[3] found two stable sites for the Ga interstitial. Using our model, we have examined both of these sites, labeled the *T* and *O* sites. At the unrelaxed *O* site, which is at the center of a *c*-axis hexagonal channel midway between Ga and N planes, the interstitial has three cation and three anion neighbors, each at a distance of about 2.1 Å. Upon relaxation, the interstitial Ga(*O*) moves 0.41 Å parallel to the *c* axis, toward the N plane. There is also considerable relaxation of these three N atoms and the three Ga neighbors so that the final Ga-Ga and Ga-N bonds are 2.40 and 1.94 Å, respectively. These are very close to the distances seen for normal bonds in bulk Ga and GaN.

At the *T* site, along the *c* axis midway between two nonbonded Ga and N atoms, we find more dramatic relaxation, with the Ga neighbor moving away from the interstitial by 0.86 Å. Because the unrelaxed geometry of this site is so cramped, the N neighbor also moves away from the interstitial, by 0.10 Å, as shown in Fig. 2. This relaxation is large; it involves primarily these two neighbors, and the energy gain is enormous, much larger than that seen at the *O* site. We find that the relaxed *O* site is 3.5 eV lower in energy than the relaxed *T* site. This makes the *T* site the less likely of the two to occur under conditions of thermodynamic equilibrium. (Bogusławski *et al.* found little potential energy difference between the sites.)

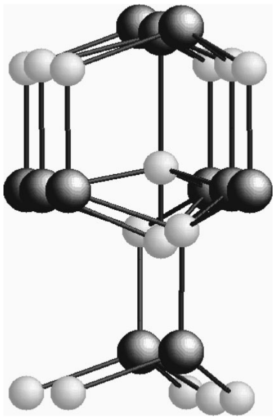

FIG. 3. The nitrogen antisite defect. A Ga atom in the center of the lowest row of galliums was replaced by a N, which moved along the *c* axis (upward in the figure), bonding with one of its N neighbors, which is itself moved upward into an interstitial position.

Our model predicts that both defects would introduce occupied and unoccupied states in the band gap. Ga(*O* or *T*) has been suggested by Bogusławski, Briggs, and Bernholc[3] as another possible candidate for the native donor, as they predict autoionizing states for these defects that are similar to those of the nitrogen vacancy. Therefore, our model disagrees qualitatively with the calculations of Bogusławski, Briggs, and Bernholc regarding the general geometry and electronic structure of the two Ga interstitials.

When a N atom is placed on a Ga site, we find that the extra N will form a strong bond with one of its neighbors, preferably the one along the *c* axis. The resulting N-N bond is 1.20 Å, 8% larger than the bond in the N_2 molecule. Further, we see a 1.0 Å relaxation of this *c*-axis N neighbor away from its original position. The net effect of this is that the originally antisite N atom essentially replaces its *c*-axis neighbor, which is forced into an interstitial position. The remaining 3 N atoms relax outward only slightly (see Fig. 3). This is very similar to but more dramatic than the relaxed geometry calculated by Bogusławski *et al.*[25] The gap states associated with this defect are all unoccupied; a doublet at $E_v+2.05$ eV and a singlet at $E_c-0.4$ eV. This is similar to Ref. 3, although our states are shifted downward with respect to theirs. An occupied singlet they identify at $E_v+0.4$ eV is in our model a valence-band resonance.

The N interstitial is predicted by both *ab initio* groups to be located along with another N atom, forming a ''split interstitial'' geometry. The two N atoms form a molecule with the center of the molecule located near the N lattice site. We find a similar geometry to be metastable for the N interstitial, and for this metastable geometry our electronic structure is composed of three closely spaced levels located 0.2 to 0.53 eV above the valence-band edge with electron occupations of 2, 1, and 0. We find a site that is 0.5 eV lower in energy, wherein the extra N atom lies in an antibonding location;

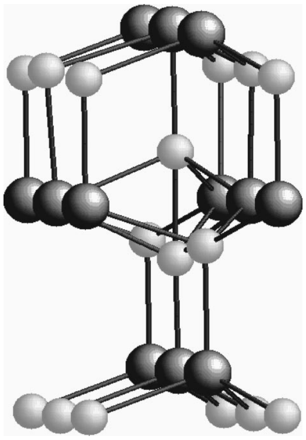

FIG. 4. The nitrogen interstitial is predicted to find its lowest-energy configuration near the *T* site; midway between two non-bonded Ga and N atoms along the *c* axis (upward in the figure). We have also found that N interstitials can lie opposite other Ga-N bonds not along the *c* axis, but these configurations are higher in energy.

bonded to a N atom directly opposite the Ga-N bond, shown in Fig. 4. This extra N is near the *T* site of the wurtzite structure and its bond lengths are 1.64 and 1.87 Å for the N-N and N-Ga bonds along the *c* axis, respectively. The other Ga-N distances are about 1.99 Å . In this configuration, the defect states in the gap are a $E_v+0.4$ and 0.75 eV and are occupied by 2 and 1 electrons, respectively.

IV. DISCUSSION

The Hamiltonian matrix elements between two Ga atoms should differ depending upon whether or not there are N atoms in their vicinity, and in a more rigorous framework than the one presented in this paper, such differences would come about via three-center (and higher-order) terms in the Hamiltonian, nonorthogonality among the localized orbitals, and the effects of the crystal field. But this is an empirical, simplified TB model for GaN, and we feel it captures the essential features of many-body effects in a very simple manner, and more importantly, in a manner with sufficient computational efficiency to permit practical molecular-dynamics simulations. Others have created environment-dependent tight-binding models for homonuclear semiconductors[26] and metals,[27] but our model is, to our knowledge, the first for a heteronuclear system.

When selecting the parameters of our model, we were faced with balancing the bulk properties against the defect properties, as might be expected. Some consequences are that the wurtzite and zinc-blende bulk moduli are calculated to be approximately 20% too large and a computed rocksalt bulk modulus which is lower than *ab initio* estimates. We tried to minimize the errors in the bulk properties because most of these have been measured experimentally whereas the defect geometries and electronic structures are not yet known. Still, we do not expect that we could achieve complete agreement with a certain set of *ab initio* defect calculations due to the vast differences between the methods used. Furthermore, there are discrepancies between the two *ab initio* studies cited in this work regarding some of the defects, particularly the antisites and the Ga interstitials. Both groups used essentially the same theoretical framework, density-functional theory within the local-density approximation (LDA). Where discrepancies existed between the *ab initio* studies cited, we favored the work in Ref. 3 as this group used a 72-atom supercell for their defect calculations, whereas the other study used 32-atom supercells.[4] This may explain why the latter group obtained symmetric geometries for the antisites, whereas the former did not. However, other differences also exist. Neugebauer and Van de Walle utilized a 60-Ry energy cutoff for their plane-wave basis set and included $3d$ electrons on the Ga atoms for most of their calculations. Bogusławski, Briggs, and Bernholc did not include the $3d$ electrons and were thus able to use a smaller 30-Ry energy cutoff.

When such issues are resolved, or preferrably, when more microscopic experimental data on native defects in GaN become available, we can revise our parameters in accordance with the new data. In the meantime, we have proceeded with our model calculations to gain insight into the possible geometries and electronic structures of larger native defects in GaN.[28]

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