First-principles Study of Hydrogen Impurity in GaN

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Abstract. *Gallium nitride (GaN) is a wide-band gap (Eg=3.4eV) semiconductor and is a candidate for high-power devices. As an impurity, hydrogen (H) plays an important role in GaN-based devices. We perform first-principles calculations to investigate the stable geometry of H impurity. We carry out the density-functional calculations within the generalized gradient approximation (GGA) using PHASE/0. We find that the bond-center site is the most stable site for H^+, whereas the trigonal channel at the center of wurtzite, where the hydrogen has three nearest Ga atoms, is the most stable for H^0 and H^-, which is consistent with the results of past theoretical studies. We discuss some details of optimized geometries and find that these geometries does not contradict with the results of μSR. We confirm that the present supercell model well describes the impurity state and conclude that the hydrogen impurity has a negative-U property in GaN, which is consistent with the past theoretical studies*

Keywords: Hydrogen, GaN, impurity

1 Introduction

Gallium nitride (GaN) is an important semiconductor after silicon. Its wide-band gap of 3.4 eV affords its special properties for applications in electronic and optoelectronic devices, i.e bright, highly efficient blue and green light-emitting diodes (LED) [1]. The photons of the emitted light have an energy similar to the value of the energy gap. GaN also is a direct band-gap. In the case of direct band gap, the optical transitions across the bandgap are "allowed" and therefore much stronger than indirect bandgaps, so the direct band gap give more light emittion than indirect band gap semiconduntor. With these advantages, GaN-based LED have started to replace light bulbs and fluorescent tubes, which means more efficiency in energy and cost reductions.

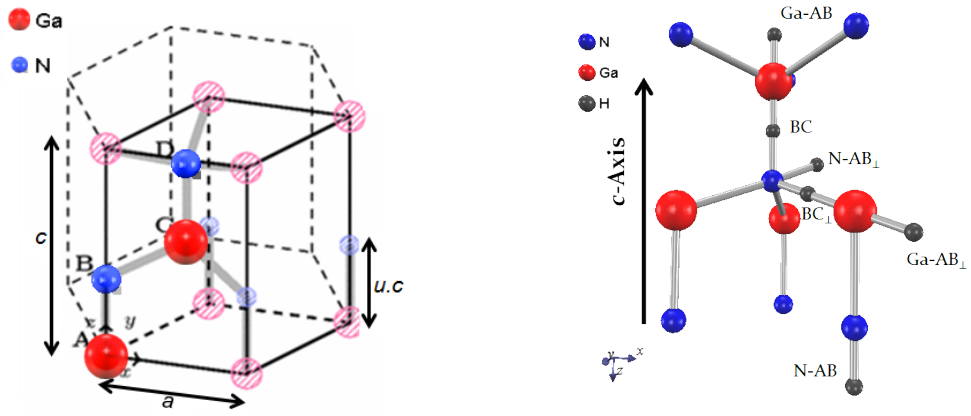
The semiconductor LED require *pn*-junction, i.e junction between *p*-type and *n*-type. However, when crystal GaN is grown by common growth techniques, it exhibits n-types conductivity. The *p*-type conductivity of GaN was initially difficult to obtain, but Akasaki and Nakamura et.al have solved it by thermal annealing and reveal that hydrogen is the important key of this problem [2,3]. Hydrogen as a common impurity in semiconductor shows very complex behavior. It has a big influence on mechanical and optoelectronic properties of several semiconductor because of its ability to passivate and compensate both shallow and deep defects. It acts as amphoteric impurity in semiconductor, which means hydrogen can acts as a donor or an acceptor [4]. Large concentrations of hydrogen appear in many semiconductor growth techniques, such as metal-organic chemical deposition (MOCVD) or hydride vapor phase epitaxy (HVPE).

In most stages of GaN-based devices fabrication are influenced by hydrogen. The hydrogen incorporated during growth of GaN to passivation the acceptors, and also in postgrowth to render the acepptors electrically active [5]. In the other words, the hydrogen atoms plays an important role in most processing step of GaN-base devices. With the role of hydrogen in GaN, it seem

to be necessary to study and investigate the relevant behavior of hydrogen in GaN. The goal of this first-principles study is to investigate the stability of hydrogen impurity in wurtzite GaN. We find the most stable geometry of hydrogen impurity in GaN and compare the stability of either positively or negatively charged states of the hydrogen atom with the neutral charge in GaN.

2 Computational Method

There are three geometry crystal structures for GaN : the wurtzite, the rocksalt and the zinc-blende (cubic). In this work, we focus on the wurtzite, which is the most stable one for bulk GaN. In order to examine the hydrogen impurity in GaN, we consider a model of one hydrogen atom in 72 atoms GaN supercell to investigate the stability geometry for charge-state of hydrogen in GaN. We carry out the first-principles calculation using PHASE/0 code, within the framework of the Generalized Gradient Approximation (GGA) and the ultrasoft pseudo-potentials. The convergence tests of the total energy with respect to the planewave energy cutoff and k-point sampling have been carefully examined. In the calculation based on the PHASE/0 the cut-off energies of the wave function and charge density are 25 and 225 Ry, respectively. A supercell geometry containing 72 host atoms, and a set of k points generated by the 2x2x2 mesh for Brillouin-zone integration. The energy convergence is within 1.0e-03 Hartree/Bohr, and remaining force in the optimized geometries is within 1.0e-03 Hartree/Bohr.



(a) Wurtzite unitcell

(b) Possible position of H in GaN

Figure 1: (a) Wurtzite unit cell of GaN consist of two atoms gallium and two atoms nitrogen, with lattice parameter a and c also the internal parameter u. (b) GaN geometry structure with six possible locations where hydrogen atom may reside, they are Ga-AB$_\perp$, Ga-AB$_\parallel$, N-AB$_\perp$, N-AB$_\parallel$, BC$_\perp$, and BC$_\parallel$,

3 Results and Discussions

3.1 The Optimized Wurtzite Structure

To study the influence of hydrogen impurity on the properties of GaN, stable structure of the wurtzite GaN has to be determined. As we can see at Fig. 1a, for wurtzite there are four atoms

per hexagonal unit cell. The unit vectors are $\overrightarrow{a_1}$=(a,0,0),$\overrightarrow{a_2}$=(a/2,$a\sqrt{3/2}$,0), and $\overrightarrow{a_3}$=(0,0,c), where a and c are the wurtzite lattice constants. The positions of gallium atom are (1/3,2/3,0) and (2/3,1/3,1/2) while the nitrogen atom positions are (1/3,2/3,u) and (2/3,1/3,1/2+u), where u is internal parameter. In the ideal wurtzite structure, the value of u is constant (u=3/8) and c/a =$1/\sqrt{u}$, all four nearest-neighbor distances are equal and all bond angles are ideal tetrahedral angles (109.5).

In present work, to get the stable structure, we calculate equilibrium geometry of the wurtzite phase, following the procedure outlined in [6]. First step, we use ideal wurtzite geometry parameter and we vary the lattice constant a to get the equilibrium of a. After that, we vary the c/a ratio while we keep the last lattice constant a and internal parameter u is ideal, we get the new c/a value. With the new c/a, we vary the lattice constant a to determine new equilibrium of lattice constant a. Finally we vary the internal parameter u by keep the value of a and c/a ratio, so we can get the equilibrium of all parameter in wurtzite geometry including u.

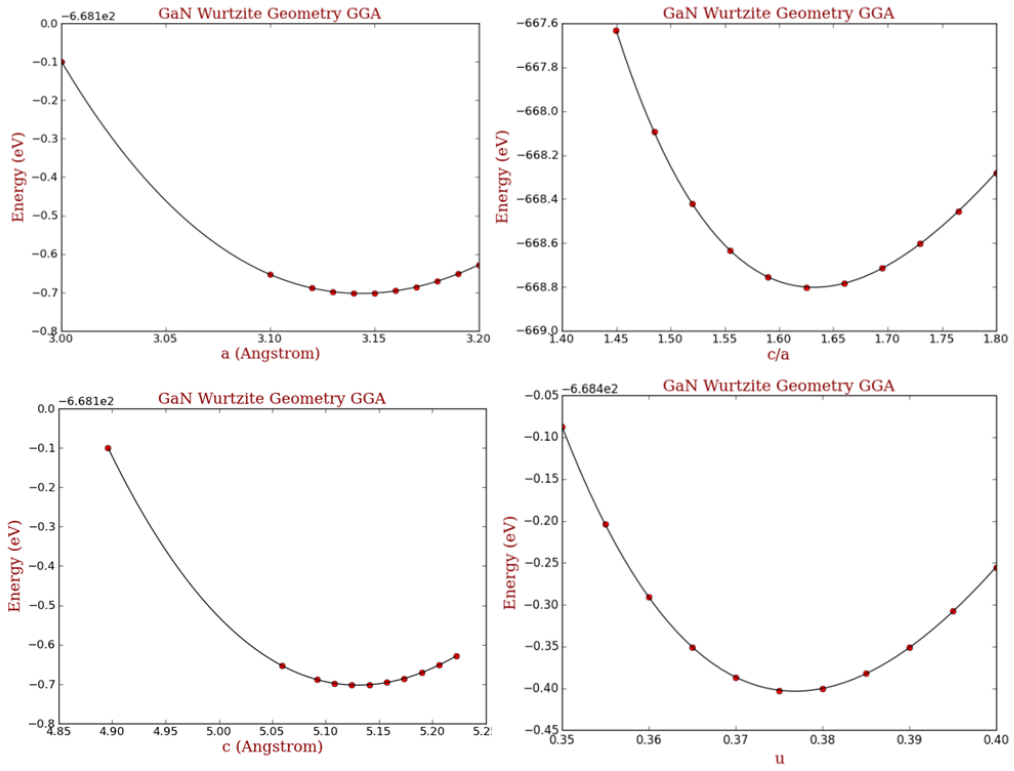


Figure 2: Total energy as a function of the latice constant a and c, c/a ratio and u for wurtzite GaN

Table 1 compares the values of the equilibrium lattice constants a, c, and of the internal parameter u resulting from the present calculation with a collection of experimental and theoretical values available in the literature. In Fig. 2, we plot the total energy versus lattice constant a,c, the c/a ratios and the internal structural parameter. With respect to experiment, our calculation lattice constant a and c as obtained using GGA is smaller by 1.16% and 0.69% respectively. After we get the stable structure, we examined several interstitial configurations of H. The equilibrium position

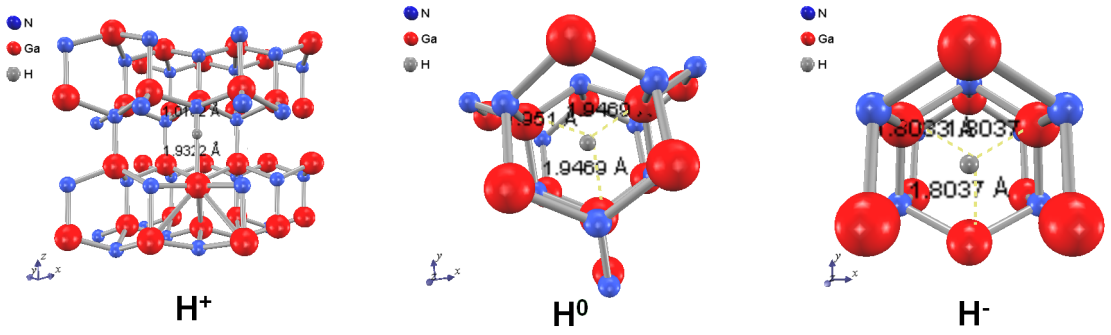
Table 1: Lattice constants a and c, c/a, internal parameter u of wurtzite GaN obtained in this works, previous theoritical calculations and experimen

Parameter	This Work	Calculations [6] [7] [8]	Experiment [6] [7] [8]
a(Å)	3.143	3.124 – 3.245	3.180 – 3.192
c(Å)	5.130	5.0 – 5.228	5.166 – 5.185
c/a	1.632	1.628 – 1.632	1.624 – 1.627
u	0.377	0.375 – 0.376	0.375 – 0.377

of H atom in the supercell of GaN is determined by the geometry optimizations with different initial positions of the H atom. Many possible sites for interstitial hydrogen were investigated for the three states, H^+, H^0, and H^-, were calculated at each site. There are six possibilities position of H atom in the supercell, as we can see at the Fig. 1b.

3.2 The Most Stable Geometry

As already mentioned before at the introduction hydrogen acts as amphoretic impurity in semiconductor, i.e. it can have positive or negative charge state. So, we examine the consequences of this amphoretic behavior of hydrogen in GaN. First we determine the most stable geometry by calculating the total energies for neutral and charge states of hydrogen in GaN. The hydrogen atoms were placed in various possible position (see Fig. 1b), then perform the self-consistent field (SCF) calculation based on density functional theory (DFT) with allowing the atoms to relax. The resulting total energies for H^+, H^0 and H^- are shown in Fig. 3.



(a) (b) (c)

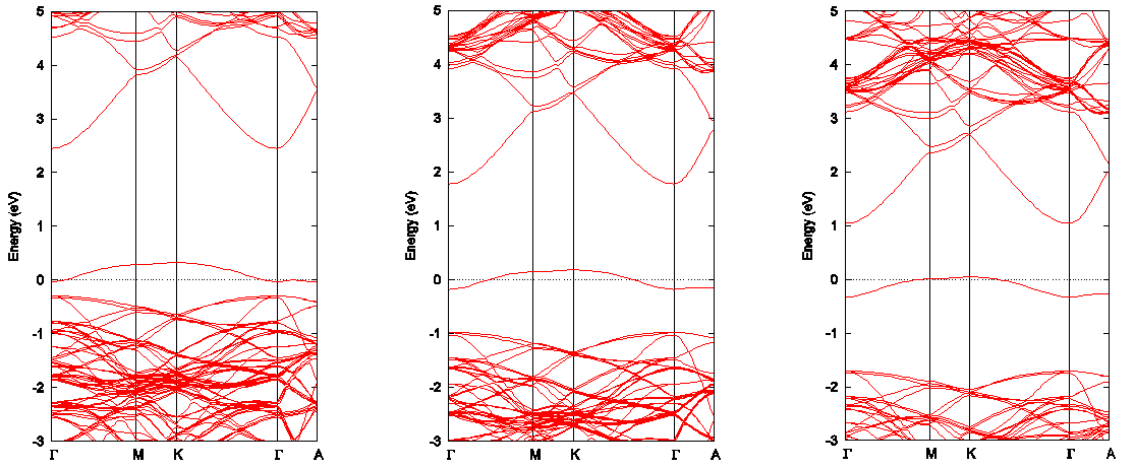
Figure 3: Configuration of the most stable geometry for hydrogen in wurtzite GaN obtained from first-principles calculation. (a)The H^+ stable at the bond center, (b) The H^0 stable at triagonal channel, and (c) The H^- also stable at triagonal channel center of wurtzite

Our results are in general consistent with those of past studies [9] [10]. Here we clarify some details of the optimized geometries. GaN is partly ionic in nature, this properties has significant influence on stable position for charge states of H. We found that the bond-center parallel to c axis ($BC_{\parallel}$) is the most stable geometry for positive charge of hydrogen (H^+) (see Fig. 3a), with

the calculated N-H bond length for this position is 1.02$\mathring{A}$ and Ga-H bond length is 1.93$\mathring{A}$. For the negative charge of hydrogen (H^-), the most stable geometry is at the center of triagonal channel (see Fig. 3c). At this geometry the hydrogen atoms has three nearest gallium atoms. Those stable geometry results for positive (H^+) and negative charged (H^-)of hydrogen in GaN are in good agreement with previous theory calculation [9] [10] and the experiment that investigate muonium (Mu) defect in GaN [12] [13]. Mu is similar or as a pseudo-isotope of hydrogen which has a very light mass ($m_\mu \simeq \frac{1}{9}\ m_p$). Those similarity and the very light mass of Mu implies to the bigger of quantum effects of Mu to give more accurate results. The neutral hydrogen (H^+) in GaN also found stable at the center of the trigonal channel (see Fig. 3b), where the hydrogen atoms has three nearest gallium atoms. The Ga-H bond length for this geometry almost same with the Ga-N bond length, about 1.95Å. The μSR experiment provides important information on the geometry [11]. We find that all the optimized geometries have trigonal symmetry, which is consistent with results of μSR ([12–14])

3.3 The Stability of Charge Hydrogen

After determining the most stable geometry of neutral and charge states of hydrogen in GaN, now we investigate which is the most stable states of hydrogen. As shown in Fig 4, the band dispersion of the impurity level is small enough to determine the energetical position of the impurity level. In order determine the stability of the system with charged states compared to the neutral one, we examine several steps as follows. In case for negative charge states, first we determine the most stable geometry structure of neutral charge state, and we have done this in the sub section 3.2. After that we calculate the total energy of the -1 charge state for the geometry optimized in the case of the neutral charge state, $E_{tot}(0)$. second step, we optimize the geometry for the -1 charge state and get the total energy, $E_{tot}(-1)$. The difference between the energies of $E_{tot}(0)$ and $E_{tot}(-1)$ is called the relaxed energy ΔE_{relax} which is negative.



(a) (b) (c)

Figure 4: The calculated band structure of GaN with hydrogen atom in three different charged states, to measure the ΔE_{relax} (a) positive half charged, (b) neutral, and (c) negative half charged.

According to the Slater's argument [15] [16] that explain if we have two systems with the same

atomic geometry and have charged states 0 and -1, then the difference in total energy between them is given as the highest occupied level energy of a system having half-negative charge with the same atomic geometry. So in the third step, we carry out calculation of the electronic structure levels for the negative half charge state and the geometry optimized for the neutral charge state, then we calculate the difference between the energies of the impurity level and the valence band maximum, is called the level energy ΔE_{level} which is negative. We can get this value from electronic band structure as seen on Fig. 4. The energy of the ΔE_{relax} and ΔE_{level} for the positive charge state can be computed in the same manner as well as negative charge.

The relative total energy of the charged states q hydrogen for the fermi energy μ is given by :

$$^{rel}E_{total}(q) = \Delta E_{relax}(q) + \Delta E_{level}(q) + \mu.q \tag{1}$$

As we can see at Fig. 5, it shows the relative total energy of hydrogen impurity in its various charge state in GaN. The Fermi level (E_F) is set to zero at the top of valence band of GaN and (E_F) changes within the calculated band-gap energy. The E_F moves through the band gap. In the beginning, the stable charge is the positive charge of hydrogen (for E_F below 1.7eV) and then changes directly to the negative one (for E_F above 1.7eV). This implies that p-type GaN, where E_F close to the valence band maximum, the positive charged H^+ is stable and H act as a donor. For the n-type GaN, where E_F close to the conduction band minimum, the negative charged H^- is favored and act as acceptor. The facts that the neutral states H^0 is never stable in this system, on the other words that the hydrogen thus effectively "self-compensates". With this results, we conclude that the hydrogen has a negative-U behavior in GaN, which is consistent with the results of past theoretical studies [9] [10].

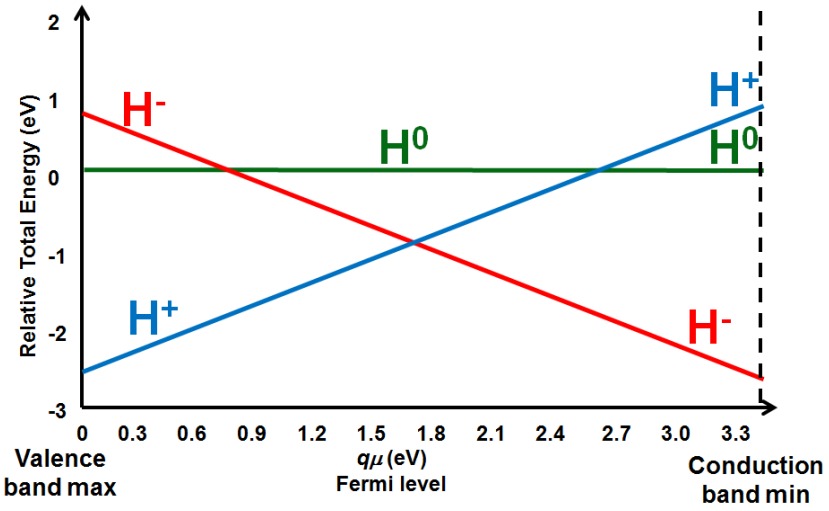


Figure 5: The relative total energies of the positively charged (H^+), neutral (H^0), and negatively charged (H^-) as a function of fermi level. When fermi level = 0, it is corresponds to the top of valence band.

4 Summary

First-principles calculations are carried out to investigate the behavior of hydrogen impurity in GaN. We find that the bond-center (BC) site is the most stable geometry for H^+ impurity whereas the trigonal channel at the center wurtzite with the hydrogen has three nearest Ga atoms is the most stable geometry for H^0 and H^-, which is consistent with results of past studies. We clarify some details of the geometries and find that our results are in good agreement with experimental results of muon. However, the calculation of the hyperfine coupling constants is necessary for further discussion in future. We clarify that the present supercell model well describes the impurity level and find that the hydrogen impurity has a negative-U property in GaN, which is consistent with the results of the past theoretical studies.

Acknowledgment

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