Density functional theory study: 
Electronic structures of RE:GaN in wurtzite

\[ Ga_{15}RE_{1}N_{16} \]

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Abstract. Gallium nitride (GaN) is a wide-band gap (E_g=3.4eV) semiconductor. Rare-earth (RE) in GaN have attracted interest due to their potential applications. Electronic structure calculations were performed for substitutional rare-earth (Pr, Er, Eu, Nd, and Dy) in wurtzite supercell GaN using density functional theory calculations within the GGA approach. Our calculations show that RE doped in GaN exhibit an indirect band gap and introduces an impurity level. We found the equilibrium bond lengths of RE-N are vary between 2.13 to 2.253\( \text{Å} \) in good agreement with structural data available for Eu and Er. We confirm that the present supercell model well describes the state of RE in GaN. Its predicts the band gap narrowing that expected to improve the optical performance of GaN.

1. Introduction

The group III-nitrides are most interesting semiconductors for the optoelectronic devices operating in the visible range. Gallium-Nitride (GaN) is one of this group which due to its wide direct band-gap of (e.g=3.4eV), strong bonding, high thermo-conductivity is considered as one of the most promising materials for optoelectronic devices, i.e Light Emitting Diode (LED) [5]. 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 band gap are "allowed" and therefore much stronger than indirect band gaps. The direct band gap gives more light emitting than indirect band gap semiconductor. Over the last two decades, GaN-based blue/UV-LED have significant development. As a solid state lamp (SSL), GaN-based LED starts to replace light bulbs and fluorescent tubes, which means more efficiency in energy and cost reductions.
Rare-earths (RE) atom doping in GaN have received wide attention because it can be used for the realization of photonic and electroluminescent devices [13]. The modifying the active layer of GaN can produce the white light within the layer itself. It could be achieved by doping the active layer with activator, i.e. RE. In particular, some RE in GaN can be used as primary color sources or mixed to obtain the full visible spectrum [10]. Moreover, GaN suffer less from temperature quenching of the luminescence than other hosts, it makes GaN is good material to realize high brightness LED with outstanding durability and lifetime [1].

To investigate the GaN with RE for optoelectronic application, we need the basic understanding of electronic structure of RE and associated optical transitions in GaN. The computational approaches have been employed for prediction of electronic structure of host materials. In this study, we investigate the electronic structures of substitutional RE in wurtzite GaN by first-principles calculations based on density functional theory. First, we calculate to optimize the structural parameters of GaN. Next we optimize the structural of RE:GaN and measure the bond lengths of RE-N in RE:GaN. Finally, we calculate and analyze the electronic structures of five RE atom in RE-doped GaN.

2. Computational Approach
We carry out the first-principles calculation using PHASE/0 code, within the framework of the Generalized Gradient Approximation (GGA) and the ultra-soft pseudo-potentials. GaN have more than one crystal structure, i.e cubic zinc-blende, wurtzite and rocksalt. In this work we use the wurtzite crystal structure of GaN, which is the most stable one for bulk GaN. The relaxation calculations of the structure (e.g., lattice constant) and atomic positions were also carried out in order to obtain more optimized data of the total energies. To minimize the defect-defect interactions, a 222 supercells of the conventional un-defected GaN system containing 32 atoms was used in calculation. The supercells of wurtzite $Ga_{16}N_{16}$, and replacing one gallium atom by RE atoms were employed (see Fig. 2). The convergence tests of the total energy with respect to the plane wave energy cut-off 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 set of k points generated by the 3x3x2 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. In this study, we consider the substitutional defects only, based on the Sanna’s work [20], which said that RE atom have preference for the cationic site in GaN.

### 3. Results

#### 3.1. The Optimized Wurtzite Structure of GaN

To study the RE doped in wurtzite GaN, first, the stable structure of the wurtzite GaN has to be determined. As we can see at Fig. 1, for wurtzite there are four atoms per hexagonal unit cell. The unit vectors are \( \overrightarrow{a_{1}}=(a,0,0) \), \( \overrightarrow{a_{2}}=(\frac{1}{2}a, \frac{1}{2}\sqrt{3}a,0) \), and \( \overrightarrow{a_{3}}=(0,0,c) \), where \( a \) and \( c \) are the wurtzite lattice constants. The positions of gallium atom are \( (\frac{1}{3}, \frac{2}{3},0) \) and \( (\frac{2}{3}, \frac{1}{3}, \frac{1}{2}) \) while the nitrogen atom positions are \( (\frac{1}{3}, \frac{2}{3},u) \) and \( (\frac{2}{3}, \frac{1}{3}, u+\frac{1}{2}) \), where \( u \) is internal parameter. In the ideal wurtzite structure, the value of \( u \) is constant \( (u=\frac{3}{8}) \) and \( c/a = \frac{1}{\sqrt{u}} \), all four nearest-neighbor distances are equal and all bond angles are ideal tetrahedral angles (109.5°).

![GaN Wurtzite Geometry GGA](image1)

**Figure 3.** Total energy as a function of \( a \) and \( c \), \( c/a \) and \( u \) for wurtzite GaN.

We calculate equilibrium geometry of the wurtzite phase following the procedure outlined in [8]. First step, we use ideal wurtzite geometry parameter and we vary the lattice constant \( a \) to get the equilibrium of \( a \). Next, we keep the last lattice constant \( a \) and internal parameter \( u \) is
ideal and we vary the $c/a$ ratio to get the new optimize $c/a$ 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.

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. 3, 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 1.13% and 0.79% respectively. in general our equilibrium lattice constants results is in good agreement with another theoretical calculations and experiment data.

**Table 1.** Lattice constants $a$ and $c$, $c/a$, internal parameter $u$ of wurtzite GaN obtained in this works, another theoretical calculations and experiment.

| Parameter | this work | calculations$^{[6, 8]}$ | Experiment$^{[2, 4]}$ |
|-----------|-----------|-------------------------|-----------------------|
| $a$ (Å)   | 3.144     | 3.124 – 3.245           | 3.180 – 3.192         |
| $c$ (Å)   | 5.125     | 5.0 – 5.228             | 5.166 – 5.185         |
| $c/a$     | 1.630     | 1.622 – 1.632           | 1.624 – 1.627         |
| $u$       | 0.377     | 0.375 – 0.376           | 0.375 – 0.377         |

3.2. Undoped GaN

**Figure 4.** Band structure and DOS for wurtzite undoped GaN. The Fermi level is set to be zero.
In Fig 4, we present the electronic band structure and total density of states (DOS) for undoped GaN. The calculations for total energy, band structure and DOS for supercell wurzite undoped GaN were performed using GGA. The supercell wurzite GaN containing 32 atoms, consist of 16 gallium atoms and 16 nitrogen atoms. The value of calculated band gap of undoped GaN is found to be direct at Γ to Γ point and equal to 2.6eV. This is in close agreement with the results of Rubio et al. [3], Vogel et al.[7], and Pugh et al.[9]. Our band gap value is smaller about 23% compared to experimental value of 3.47eV because of the well known underestimation of DFT calculations using GGA as reported in other work by Simanovskii et.all [15]. However, it is widely accepted that the GGA electronic band structures agree qualitatively with experiments work as concerns the ordering of the energy levels and the shape of the bands [18].

Table 2. Calculated band gaps undoped GaN in wurzite supercell structures compared to other theoretical calculations and experiments.

| Parameter          | this work calculations | Experiment     |
|--------------------|------------------------|----------------|
| $E_g (\Gamma_v - \Gamma_c)$ | 2.6 (eV)              | 3.474 – 3.507 (eV) |

3.3. The Optimized Structure of RE:GaN
In Table 3, the optimized structure of RE:GaN from PHASE/0 calculation using 2x2x2 supercells (Fig 2) consisting of one rare earth atom, fifteen gallium atoms and sixteen nitrogen atoms are listed in Table 3. One RE atoms substituting for gallium atom continue to be tetrahedrally coordinated. The lattice relaxations make the nitrogen atoms move away from RE atom to accommodate this larger atom at the gallium site (Fig 5). The RE-N bond length vary from 2.133 to 2.253 Å. These results are in good agreement with the available data from extended X-ray absorption fine structure (EXAFS) measurements [14, 12]. The calculated bond lengths are also in good agreement with those calculated by K.C Mishra et al. [19] and Filhol et al.[17] using GGA approach and same wurzite structure.

Figure 5. The atomic structure for RE:GaN, the lattice relaxations surrounding the RE atom lead to longer REN bonds (in this case RE=Er)
Figure 6. Band structure for RE:GaN. (a) Er:GaN, (b) Pr:GaN, (c) Eu:GaN, and (d) Nd:GaN. The Fermi level is set to be zero.
Table 3. Optimized structure for RE:GaN. Ga$_{16}$N$_{16}$, and replacing one Ga by RE atom, Ga$_{15}$XN$_{16}$, X = Pr, Er, Eu, and Nd. The local relaxation of the atom around the RE result in the following X-N distances

| No | Supercell | $d_{X-N}(\text{this work})$ | $d_{X-N}(\text{another calculation})^{[19]}$ | $d_{X-N}(\text{Experiment})^{[14]}$ |
|----|-----------|-----------------------------|---------------------------------------------|-------------------------------------|
| 1  | Ga$_{15}$N$_{16}$Pr | 2.165-2.236 | 2.262-2.295 | 2.23 ± 0.06 |
| 2  | Ga$_{15}$N$_{16}$Er | 2.132-2.188 | 2.152-2.178 | 2.3 – 2.5 |
| 3  | Ga$_{15}$N$_{16}$Eu | 2.141-2.200 | 2.260-2.304 | |
| 4  | Ga$_{15}$N$_{16}$Nd | 2.160-2.253 | 2.246-2.278 | |
| 5  | Ga$_{15}$N$_{16}$Dy | 2.133-2.192 | 2.165-2.194 | |

3.4. RE:GaN electronic structure

In this section, we present the electronic structure calculations of RE:GaN. We find that our results for the band structure and density of states-DOS (the DOS is not shown here) in general are consistent with another past theoretical studies [20] [19]. Here we clarify some details of the electronic properties of RE:GaN. Figures 6 show the band structure for Er:GaN, Pr:GaN, Eu:GaN and Nd:GaN respectively. Obviously, GaN is a direct band gap semiconductor, in contrast with RE:GaN which is exhibits an indirect band gap. For Er:GaN exhibits an indirect band gap of ±2.6eV with conduction band minimum ($C_{B_{min}}$) at point Γ and valence band maximum ($V_{B_{max}}$) at point M (Fig 6.a). For Pr:GaN exhibits an indirect band gap of ±2.7eV with $C_{B_{min}}$ at point Γ and $V_{B_{max}}$ at point K (Fig 6.b). For Eu:GaN (Fig 6.c) and Nd:GaN (Fig 6.d) have same trends with Pr:GaN, exhibits an indirect band gap with $C_{B_{min}}$ at point Γ and $V_{B_{max}}$ at point K and the calculate indirect band gap about ±2.6eV and ±2.7eV respectively.

The dopant RE also introduces an impurity level at 0.4eV, 1.7eV, 1.2eV and 1.2eV above the $V_{B_{max}}$ within the energy gap for Er,Pr,Eu and Nd respectively, which is make the band gap narrowing. Most of them make the energy band shift towards the low energy regions, this can be also clearly seen from Fig. 6. The band gap narrowing RE:GaN facilitate the optical transition between the different levels of RE:GaN which is also confirmed experimentally by Majid et al. [21]. This properties will help improve the optical performance of the GaN.

4. Summary

We have investigated the rare earth doped in GaN using first-principles calculations based on density functional theory. The lattice relaxations surrounding the rare earth atom make the bond length of REN lead to be longer. We find that the dopant introduces the impurity level and the energy band shifts towards to the low energy regions. The impurity level provides the band gap narrowing (BGP) of RE:GaN which will help improve the optical performance of the GaN, which is this results consistent with the results of the past theoretical studies. However, the calculation of the optical and magnetic properties is necessary for further discussion in future.

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