The Calculation Study of Electronic Properties of Doped RE (Eu, Er and Tm)-GaN using Density Functional Theory

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Abstract. The calculation of the structure and electronic properties of Rare Earth (RE) at the wurtzite Gallium Nitride (GaN) based on DFT has completed. GGA approximation used for exchange correlation and Ultra soft pseudo potential too. The stability structure of GaN is seen that difference lattice parameter 11% lower than another calculation and experiment result. It is shown the stability structure GaN have direct band gap energy on Gamma point hexagonal lattice Brillouin zone. The width $E_g$ is 2.6 eV. When one atom Ga is substituted with one atom RE, the bond length is change 12 % longest. A in good agreement with theoretical doping RE concentration increases, the edge of energy level shifted towards to make the band gap narrow which is allow the optical transitions and help to improve the optical performance of GaN. The RE doped GaN is potentially applicable for various color of LED with lower energy consumption and potentially energy saving application

1. Introduction

Lighting technology is widely used in daily life. The huge growth of population and advanced life demand equipped developing with qualified lighting and saved. New materials using RE over significant progress in the development of optoelectronic technology and photonic like element Neodymium (Nd) which can emit a laser and phosphorus in the solid state, Er or Tb for displays and lighting, Er or Pr used in fiber optics for telecommunications [1], so that the use of RE also potentially be applied to the manufacture of LEDs. While blue LED GaN-bassed is made for the first time in 1971 by Jaques Pankove at RCA laboratories. In the mid-1990s, a researcher named Shuji Nakamura of Nichia Corp company, demonstrated a blue LED GaN-bassed for the first time with high brightness (high brightness GaN-based blue LED) [2]. The discovery cause the revolution of lighting from incandescent bulbs in the era of Thomas Edison into LED based that certainly provides a high level of efficiency and tremendous saving both in energy and cost.

The main material of LED lights currently is based on semiconductors category III-nitride, one of them is a Gallium Nitride (GaN). GaN is a semiconductor that has wide and direct band gap (direct wide band gap) [3]. With the characteristic, GaN is a semiconductor that is appropriate for optoelectronic applications, one of them is LED. The first approach is the color mixing by configuring three single colors LED (Red-Green-Blue) and the second approach is to combine LEDs with conversion of emission color materials in whole or in part [4].
2. The Calculation Study Electronic Properties of GaN RE using DFT

2.1. Many Body Problem
The problem of quantum systems with many particles number is called Many Body Problem. Then the equation is done by completing the configuration of the ground state of the electrons first, then calculate the energy of the system configuration, and finally completed the calculation of core movement. Separation of the movement of electrons and nuclei calculation is known as the Born-Oppenheimer approach [5]. Hamiltonian becomes:

\[ H = \frac{1}{2} \nabla^2 + \sum_{i} \frac{1}{|r_i - r_j|} + V_{\text{ext}} \]

(1)

\[ \dot{V}_{\text{ext}} = -\sum_{i} \frac{Z_i}{|r_i - R|} \]

(2)

2.2. Hohenberg-Kohn Theory
The big idea of the DFT is that the wave functions of many particles, can be defined as a function of the electron density. It comes from the idea that for a certain value, it will represent a wave function well (unique). In general theory of Hohenberg-Kohn stated:

First, a wave function of the ground state uniquely defined by a function of the density in the ground state. In mathematical equation becomes:

\[ \psi_{n_0}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \psi[n_0(\mathbf{r})] \]

(3)

It is most essential in the DFT. As a consequence, the value expectations of the ground state (Ground State) for all is also a function of [5]

Secondly, the expected value of the total energy of the ground state which is expressed in:

\[ E_{n_0} = E[n_0] = \langle \psi[n_0] | \hat{H} | \psi[n_0] \rangle \]

(4)

Energy value has a principle of variation which,

\[ E[n_0] \leq E[n] \]

(5)

Applies,

\[ E[n_0] = \langle \psi[n_0] | \hat{H} | \psi[n_0] \rangle \leq \langle \psi[n] | \hat{H} | \psi[n] \rangle \]

(6)

This principle can be utilized, that minimizes the expected the total energy value eV an external potential \( V_{\text{ext}} \) can be done with a functional derivative of the expectation value of the electron densities

2.3. Total Energy
DFT is a method for calculating the electronic structure of a system of atoms, molecules, or material. In general, the total energy of an electron systems are defined:

\[ E_n = \langle \psi[n] | \hat{H} | \psi[n] \rangle \]

(7)

And Hamiltonian \( \hat{H} \) can be written:

\[ \hat{H} = \hat{T} + \hat{U} + \hat{V} \]

(8)

In this case \( \hat{T} \) the kinetic operator, \( \hat{U} \) the operator of potential interactions between electrons, and is the operator of potential interactions between the electrons with the outside. Total electron energy becomes:

\[ E[n] = T[n] + U[n] + V_{\text{ext}}[n] + E_{\text{xc}}[n] \]

(9)
2.4. Kohn-Sham Equation
The most stable state is obtained when the system is in a state of minimum energy. Hohenberg Kohn theory of the equation (12), the minimum total energy directly correlated with minimum electron density. So that minimum energy can be obtained using the equation lagrange multiplier by lowering the equation (9) to the electron density $n(r)$. By entering these constraints, the minimization of the total energy equation becomes:

$$\frac{\delta}{\delta \rho}(E[n] - \sum \lambda_i \int \phi_i^* \phi_i^d \, d^3r) = 0$$

(10)

2.5. Self Consistent Field (SCF)
Total electron density is the sum of the square of the orbital all off the function. KS then to solve this equation, we need an educated guess electron density value which is then used to solve the equation KS. SCF cycle is shown in the algorithm in Figure 1.

2.6. Pseudopotential
Pseudo potential method gives the idea that electrons can change and interact are just part of the outer electrons (valence electrons). With a core electron approaches that have been fixed, then this method provides a solution by replacing the external potential $V_{ext}^{pseudo}$ at the core electrons with pseudo potential and wave function with pseudo wave function. So the equation that needs to be resolved:

$$\left(-\frac{1}{2} \nabla + v_{ee} + v_{ext}^{pseudo} + v_{xc}^{pseudo}\right)\psi^{pseudo}_i = \lambda_i \psi^{pseudo}_i$$

(11)

2.7. Exchange Correlation Energy
2.7.1 Local Density Approximation (LDA). LDA is the basis and the simplest of all approaches to energy $E_{xc}$. The main idea of the LDA is the charge distribution in a region are uniform and localized. $E_{xc}$ so that energy can be written:

$$E_{xc}^{LDA}[n] = \int n(r) v_{xc}[n(r)] d^3r$$

(12)
2.7.2 **Generalized Gradient Approximation** (GGA) The difference from the concept of LDA, is information that is used not only on data from the electron density \( n(r) \) at position \( r \), but also retrieve information from the gradient changes electrons density in the position. Then the \( E_{xc} \) energy becomes:

\[
E_{xc}^{GGA}(n_\alpha,n_\beta) = \int (n_\alpha \cdot n_\beta \cdot \nabla n_\alpha \cdot \nabla n_\beta) d^3r
\]

(13)

3. **Method**

This study uses a program package to PHASE / 0 [6]. The program is able to perform the calculation for the extended case through super cell scheme. Program PHASE / 0 capable of calculating the energy value of a system in an atomic scale, also called SCF calculation, to determine the condition of the ground state of the system. In addition to the calculation of SCF, PHASE / 0 is also capable of performing calculations to see either the electronic structure of Band Structure and Density of States (DOS), the spin density distribution and electron density.

Firstly, determine the model structure of solids that will be calculated (the position of atoms, crystalline form, and the lattice constants). Calculate the charge density by using SCF cycle. SCF cycle can be seen in Figure.2

![Figure.2 Working Cycle on Phase](image)

This study uses a wurtzite crystal structure, because it is the most stable structure among other GaN structures. Figure.3 showed the smallest cell unit wurtzite GaN crystal structure consisting of four atoms, two Ga atoms and two N atoms has a cell unit vector unit is \( \mathbf{a}_1 = (a, 0,0), \mathbf{a}_2 = (a/2, \sqrt{3}/2, 0) \) and \( \mathbf{a}_3 = (0,0, c) \) where \( a \) and \( c \) is the length of the lattice parameter wurtzite. GaN atomic coordinate position is \( (1 / 3, 2 / 3, 0) \) and \( (2 / 3, 1, 2) \), while the position of the N atom is \( (1 / 3, 2 / 3, u) \) and \( (2 / 3, 1, 3, 1 / 2 + u) \), where \( u \) is the internal parameters. In ideal wurtzite, is a constant value \( u \) \( (u = 3/8) \) and the value. To obtain the value of the optimal parameters for \( a, c, c/a \) and \( u \), then the geometrical structure optimization process unit cell of GaN.

![Figure.3 Wurtzite unit cell geometry and consists of two gallium atoms (red) and two nitrogen atoms (blue), with lattice constants a and c as well as the internal parameter u.](image)
In RE: GaN single Ga atom is substituted by one atom RE, so the calculation of RE: GaN using 
\( \text{Ga}_{1-x}\text{RE}_x\text{N} \) configuration. In Figure.4 super cell shows a model by substituting a single atom with one atom RE: GaN. This study uses super cell size of 32 atoms, with the configuration \( \text{Ga}_{1-x}\text{RE}_x\text{N} \) in super cell 32 atoms (\( x = 0.0625 \)).

![Image](image.png)

Figure. 4 Geometry wurtzite GaN super cell with substitutions 1 Ga atom by atom RE

\( E_{xc} \) energy type approach is used in this calculation use cut off wave function 25.00 Ry and cut off the charge density is 225.00 Ry. This calculation uses meshing methods for the integration of the brillouin zone with values for super cell k-point 2x2x2. SCF calculations done in a relaxed position with the convergence of energy limit 1.0e-03 Ha tree / Bohr and bounds in the style of the geometry optimization of 1.0e-03 Ha tree / Bohr.

4. Result

4.1. Geometry Structure Optimization

In this study used the crystal structure is wurtzite GaN. The procedures performed in this geometry optimization process following the procedures in reference C. Stamp et al [8]. Figure.5 show visualization of the modeling results unit cell GaN.

![Image](image.png)

Figure .5 GaN modelling results using PHASE / 0 in wurzite structure optimization forum for lattice parameter values a and c, c / a ratio and internal parameter u for wurzite GaN

4.2. Pure GaN

In the plot shown Figure.5 total energy as a function of the lattice parameters a and c, the value of c / a ratio as well as the internal parameter u. Tabel.1 shows the comparative results of the calculation of the geometrical structure optimization unit cell GaN with experimental data and other calculations. The
calculation in this study demonstrates the value corresponding compared with experimental data and other calculations, even for internal parameter \(u\) showed identical results with experimental data.

Table 1. Comparison of the calculation results wurtzite GaN structure optimization geometry \(a\) and \(c, c/a\), internal parameter \(u\) with the results of other calculations and experimental data

| Parameter | This work | Others Calculation | Experiment |
|-----------|-----------|--------------------|------------|
| \(a (\text{Å})\) | 3.142 | 3.124 - 3.245\(^a\) | 3.180 - 3.192\(^b\) |
| \(c (\text{Å})\) | 5.123 | 5.0 - 5.228\(^a\) | 5.166 - 5.185\(^b\) |
| \(c/a\) | 1.630 | 1.622 - 1.632\(^a\) | 1.624 - 1.627\(^b\) |
| \(U\) | 0.377 | 0.375 - 0.376\(^a\) | 0.375 - 0.377\(^b\) |

\(^a\)Ref [3,8] \(^b\)Ref [8]

![Graphs](image.png)

Figure 6. Total energy of the system as a function of cell units and value lattice parameters \(a\) and \(c\), the ratio of \(c = a\) and \(u\) internal parameters for wurtzite GaN

4.3. GaN Doped RE

Calculation of total energy of the system, and the energy band structure and DOS of the system using the super cell 2x2x2 containing 32 atoms consisting of 16 atoms of gallium and 16 atoms of nitrogen, Figure 7 an energy band structure of pure GaN. From these images are shown GaN having a band gap energy directly (direct-band gap) in both the conduction band minimum (\(\text{CB}_{\text{min}}\)) and the valence band maximum (\(\text{VB}_{\text{max}}\)) are at a point with a difference of 2.6 eV.

The results of calculation of the energy band gap is smaller by about 26% compared with experimental data [8, 2]. This value also occurs in other theoretical calculations that use the same approach to energy exchange, ie GGA [7]. This occurs because of the underestimation factor calculation that occurs in DFT calculations using the GGA as reported in other work by Simanovskii et al [5].
The pattern of the electronic structure of GaN energy band gap of the calculation results, proving that the material properties of GaN has a direct wide band gap. These properties indicate GaN material particularly suitable for optoelectronic applications, such as LEDs.

Table 2 Comparison of the energy band gap calculation results of theoretical calculations using the GGA with experimental data

| Parameter | This Work | Others Calculation | Experiment |
|-----------|-----------|---------------------|------------|
| Eg (eV)   | 2.6       | 2.3±1.9±1.7±       | 3.474-3.507d |

GaN crystal structures form four bonds between gallium and nitrogen atoms form a tetrahedral coordination. The results of structural optimization in the previous step shows in Table 3.

Table 3 Comparison of the long bond-length RE-N on structure optimization RE: GaN

| No | Super cell | d_{RE-N} (Å) This Work | d_{RE-N} (Å) Others Calculation | d_{RE-N} (Å) experiment |
|----|------------|-------------------------|---------------------------------|-------------------------|
| 1  | Ga_{15}N_{16}Eu | 2.1435-2.2009 | 2.260-2.304a | 2.3-2.5d |
|    |             |                        | 2.00-2.21b                    |                         |
| 2  | Ga_{15}N_{16}Er | 2.1267-2.1887 | 2.152-2.178a | 2.23 ± 0.06c |
|    |             |                        | 2.14-2.20b                    |                         |
| 3  | Ga_{15}N_{16}Tm | 2.1273-2.1281 | 2.15-2.30b | |

In previous calculations show the structure of GaN without doping RE with the wide energy gap of 2.6 eV. Further calculations to investigate the state of the electronic structure in terms of the energy band gap structure as well as the state of DOS Table 4 and Figure. 8, 9 and 10.
Table 4 Comparison of wide band gap (band gap) and the impurity band due to the influence of RE dopant in GaN

| No | Dopant | Atom Number | Wide of band gap (eV) | Impurity level VB<sub>max</sub> (eV) |
|----|--------|-------------|-----------------------|----------------------------------|
| 1  | Eu     | 63          | 2.6                   | 1.22                             |
| 2  | Er     | 68          | 2.63                  | 0.51                             |
| 3  | Tm     | 69          | 2.64                  | 0.35                             |

Figure 8 Energy band structure and DOS for Ga<sub>15</sub>N<sub>16</sub>Eu

Figure 9 Energy band structure and DOS for Ga<sub>15</sub>N<sub>16</sub>Er
Figure 10 Energy band structure and DOS for Ga$_{15}$N$_{16}$Tm

Figure 8, Figure 9, Figure 10 showed the same trend, namely a change in energy band structure in the form of indirect band gap formation and an impurity band. RE doping in GaN also resulted in the formation of an impurity band located between CB$_{\text{min}}$ and VB$_{\text{max}}$. Pita impurity gives an advantage, since the narrowing of the energy band gap and this allows the optical transitions, which helps improve the optical performance of GaN.

5. Summary
The results of electronic structure calculations RE ions in GaN showed a structure stability RE: GaN in tetrahedral coordination with relaxation RE-N bond lengths varying between 2.1-2.2˚A, this result is consistent with the data structure of the results of other calculations and experimental data EXSAF. RE: GaN also indicates a change in the electronic structure, which resulted in the band gap energy into indirect (indirect band-gap) and the formation of an impurity band with varying sizes for each dopant RE. Impurity band that forms resulted in a narrowing of the energy band gap which facilitates the optical transitions in materials that are expected to improve optical performance on GaN. Addition of RE dopant concentration in the GaN shows a shift in the boundary of the valence band is getting towards the low energy area, thus making the material more stable at room temperature.

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