Electronic Structure and Impurity Level Location of Rare-Earth (Ce, Pr, Nd, Dy) Doped GaN : GGA Approximation

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Abstract. Electronic structure and impurity level location of rare-earth (RE) doped GaN have been investigated. Based on density functional theory GGA Approximation, the electronic structure of GaN and GaN:RE are calculated in hexagonal structure. The lattice parameter, bond length of Ga-N and the tetrahedral angle of N-Ga-N show the 3% change from experimental results. When we substitute Ga to RE in the GaN structure, the bond length changes 12% longer with the equilibrium bond length of RE-N varies between 2.1382 Å - 2.2428 Å. The ionic radii of RE larger than Ga, it will affect to tetrahedral angle which vary from 112.68° − 113.60°. In the electronic properties calculation, the pristine GaN has direct band gap 2.58 eV. The impurity energy level of Ce, Pr, and Nd are detected in the band gap while Ce level lies near conduction band minimum and the impurity level is contributed by 4f electron states. By this, the 4f energy can explain the luminescence process from rare-earth atoms to host materials. The band structure of GaN:RE is expected to allow optical transition in IR-UV emission range. GaN:RE has high potential to be applied to lower energy of light emitting diodes and energy-saving devices.

Keywords: GaN, Rare-Earth, electronic structure, GGA approximation

1. Introduction
Semiconductor III-V has been used for high performance light emitting devices. This is the most recent revolutionary lighting advancement for saving and lower energy. At the room temperature, III-nitrides materials have the direct transition with energy band gap ranging 1.9-6.2 eV for InN, GaN, and AlN[1][2]. Blue light-emitting device was found by Nakamura et al. using nitride materials[3][4]. Magnesium as an impurity transition contributed to blue light in the p-semiconductor layer, this performance has high efficiency several times than SiC LED[5]. The significant progress is developed from blue-UV spectra of InGaN mixed with a yellow phosphor to get white light. The light is generated within active layer of InGaN due to pair recombination e-h injected impurity. Addition impurities materials on the host material makes changes to the band’s energy.

Rare-earth (RE) has unique properties since strong visible wavelength was explored when GaN doped RE[6][7]. The energy level 4f has high energy that the position is relative to valence band and conduction band of host materials[8][9]. Energy of the f shell RE contributed to
narrowing band energy, this is detected on RE doped which has high peaks spectral[10]. For example Eu atom has 6 electron in f shell, these produce red emission when doped in GaN[11]. GaN:Ce and GaN:Pr clearly has red emission with the number of electron in f shell smaller [12][13]. Another color has found in GaN:Tm (blue) and GaN:Eu (green) [14]. Sharp peak energy was shown in the transition $^5D_0 \rightarrow ^7F_2$ by RE ions doped which produce IR spectrum[15]. It indicates that valence electron of RE excited to host materials.

Basic understanding of electronic structure of RE doped GaN is needed to explain the wide range energy band. In this paper, investigation the electronic properties of GaN doped RE is clarified based on DFT calculations. We study RE elements including Ce, Pr, Nd, Dy to complete basic understanding impurity level location to host materials. In Sec II. the computational model which is used will be presented. In Sec. III. analysis of structure and electronic behavior of doped RE are also studied to understand the energy structure of impurity. Finally, the summary will be presented in Sec. IV.

2. Computational Model

PHASE0 is used to calculate electronic structure of pristine GaN and GaN:RE[16]. GGA Approximation was applied for exchange-correlation energy, $E_{xc}$, to give rather accurate result for the systems[17]. The calculations are carefully calculated with Ultrasoft pseudopotential, which the cut-off energy for wave functions is 25 Ry and cut-off energy for charge density is 225 Ry. The structure evolution is set with atomic force $0.1^{-3}$ Hartree/Bohr. K-points generate $2 \times 2 \times 2$ mesh generation for geometry optimization. Convergence of total energy is carefully examined to the cut-off energy and k-point sampling. Both GaN and GaN:RE are modeled in hexagonal structure 32 atoms, the most stable in bulk structure. First, optimization of unit cell hexagonal structures are performed with four atoms per hexagonal unit cell. Group III elements are placed on (0,0,0) and (0,0.6667,0.3333,0.5). Nitrogens is placed on (0,0,u) and (0.6667,0.3333, u + 0.5), which u is internal parameter. This calculation uses vectors $\mathbf{a}=(a,0,0)$, $\mathbf{b}=(0.5a,0.866a,0)$, and $\mathbf{c}=(0,0,c)$, which $a$ and $c$ are lattice parameter of hexagonal structure[18]. These parameters are related by $(\frac{c}{a})^2 = \frac{4}{5} = \frac{8}{5}$.

![Figure 1](image.png)

**Figure 1.** Model of hexagonal structure in supercell 32 atoms of Ga$_{15}$N$_{16}$Dy. The RE has clearly four bonds of N atoms in the tetrahedral angles.
The optimal structure of hexagonal can be achieved with the unit cell volume parameter $V$. The independent parameters $V$, $\frac{c}{a}$, and $u$ should be optimized as done by Stampfl et. al.[19]. In the first step, the ideal parameters of hexagonal structure are used and combined with varying lattice parameter of $a$ to gain equilibrium value of $a$. Next, vary the ratio of $\frac{c}{a}$ while remain keeping the ideal of $u$ and the last lattice constant of $a$. For the second time, vary parameter of $a$ with control the ratio of $\frac{c}{a}$ to gain equilibrium of $a$. With keep retain ratio of $\frac{c}{a}$ and the last value of $a$, find the equilibrium of $u$ by varying them. Finally, calculate the unit cell volume $V$ hexagonal structure that consist of two hexagonal closest packed sublattices. RE atom substitute Ga site as illustrated in Fig. 1. Experimental result and theoretical studies have found that RE tend to occupy cation site, by binding four N atoms[20]. The composition RE on GaN structure written as $Ga_{1-x}RE_xN$ $(0 \leq x \leq 1)$, $x$ is the RE dopant concentration.

3. Result and Discussion

On the last study, we clearly explain the geometry structure of pristine GaN and GaN:RE in hexagonal structure. The lattice parameter, bond length, and tetrahedral angles have slightly changed on the GaN case. When RE is substituted Ga site, the N atoms can bind strongly and keep the position stability of the RE, thus affecting only the crystals conditions around the RE. The bond length of RE-N is longer than Ga-N because the RE radii is larger than Ga[21]. The average bond length of Ce-N, Pr-N, Nd-N, and Dy-N are sequentially 2.206 Å, 2.192 Å, and 2.165 Å. By the average of Ga-N bond length is 1.9266 Å , the bond length ratio of RE-N:Ga-N is 1:0.879. The tetrahedral angles has slightly changed in the GaN:RE structure with the largest deviation from a stable tetrahedral angle is N-Ce-N with 113.66°. The ratio tetrahedral angle GaN:Ce with GaN is 1:0.961. This ratio shows that RE is stable in the hexagonal structure of GaN.

Energy from RE affects the electronic structures of host materials. It may be used to determine the narrowing band gaps near the IR-visible light. For pristine GaN the fermi energy $E_f$ is 0.189 eV and the highest occupied band energy (vbm) of GaN is detected 0.085 eV, the electrons fill the lowest energy level. Band gap energy for pristine GaN shows 2.58 eV, it is 19.38% smaller than experimental result. Band structure is also found in direct band gap obtained with CBM and VBM lie on $\Gamma$ – $\Gamma$ points[18]. It is because DFT calculation of GGA approximation underestimate. Calculation with Hubbard U provides accurate results by considering Coulomb interaction.

Energy transfer is obtained when the excitation of the impurity becomes unoccupied, potentially use 4f energy. The density of states (DOS) for GaN:Ce, GaN:Pr, GaN:Nd, and GaN:Dy are shown in the Fig.2, which $E_f$ was set to be 0.0 eV for convenience. In this work, the ion charge of RE element is zero. The impurity energy of RE was found between conduction band and valence band on the GaN:Eu, GaN:Er, and GaN:Tm[20][21]. The conduction and valence energy of GaN:Ce was shown in the straight black line which impurity of f shell lies near conduction. GaN:Pr was shown in red dash line that indicates the position of valence energy move closest to impurity of f shell Pr. When the number of RE atom is larger, the position of valence approach to impurity and stay away from conduction, indicated by GaN:Dy which has the number of electron 4f$^9$. When the RE ions are given charge, Ce$^{+3}$, Pr$^{+3}$, that can trap holes from the valence band and may act as a hole donor in GaN. The position of Pr$^{+3}$ energy below the conduction band[9]. In the band structure calculations, the valence band maximum of GaN:Ce, GaN:Pr, and GaN:Nd ware detected in the K-point and conduction band minimum in $\Gamma$. The band structure will be discussed later.

4. Summary

The optimum structure of pristine GaN has slightly changed 2% from experimental result. When the pristine GaN structure was doped with RE, the lattice parameter, bond length and...
tetrahedral angles are stable in the hexagonal structure of GaN:RE, which four N atoms bond around RE atom in tetrahedral angles. In the calculation of electronic properties, the GaN has direct band gap 2.58 eV. It is smaller than experimental result (3.4eV). That calculation is required Coulomb interaction in the calculation to get high performance which study later. When the RE atom was substituted in the Ga site, the impurity energy was found between conduction band and valence band of host material. With this scheme, it can be started to explain optical and electronic properties RE doped GaN. Charged ions of RE is interested when placed in the host materials [9].

5. Acknowledgements
MW thanks to FMIPA ITB for financial support through the research. GRID LIPI High Performance Computing for numerical calculations were performed. Finally, MW thanks to MS for all encouragement and great support. Lets maintain this enthusiasm last forever. So, will you marry me?

6. References
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Figure 2. The DOS of GaN:RE which denoted by line colors GaN:Ce (black), GaN:Pr (red), GaN:Nd (green), and GaN:Dy (blue). The impurity of RE was clearly found between conduction dan valence band of host materials.
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