Electronic Properties of Rare-Earth Doped α-GaN

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Abstract. We carry out DFT calculation to study electronic properties of rare-earth (RE) doped α-GaN. GGA approximation and ultrasoft pseudopotential used in this calculation. The bond length and tetrahedral angle of pristine α-GaN are slightly changed. The direct band gap of α-GaN was detected at 2.56 eV, this is 1 eV lower from experiment. Electronic structure measurement is also performed for RE doped GaN (RE= Pr, Eu, Er, Gd and Tm), which the configuration is Ga₁₋ₓNₓREₓ (x=0.125). The bond length of Ga-RE is vary from 2.12-2.23 Å. The impurity energy is found relative between conduction bands and valence bands of host materials.

1. Introduction

In this recent decade, semiconductor III-V is used for electronic materials, magnetic and optical devices, particularly GaN [1][2]. Since Nakamura has found blue light emitting diodes (LED) from thin layer of GaN [3], these is possibly used in the optical devices operating ultraviolet until visible light. GaN has wide direct band gap 3.4 eV. This band gap is much stronger and produce more light emitting than indirect band gap. LED based on GaN starts to replace light bulbs or fluorescent lamp with more efficient and low cost energy.

Rare-earth (RE) doping GaN has gained more attention as an electroluminescent devices (ELDs). Modifying the active layer of GaN with activator RE can impact-excite RE dopants and produces emission of light. Visible spectrum is obtained by photoemission from excite RE states in GaN. GaN:Pr and GaN:Eu have been shown to produce light emission in red color (Pr at 650 nm and Eu at 621 nm)[4][5]. Green and blue are detected on the Tm (at 477 nm) and Er (at 537 nm) doped [6][7][8]. Mixed colors are created from combining primary colors [9]. RE doped GaN is good to generates high brightness LED.

In this paper, basic understanding of the electronic properties and optical transition RE doped GaN are needed to investigate photoemission. This requires first principle calculation based on density functional theory (DFT) to predict electronic structure from RE to host material GaN. First, optimize structure of pristine α-GaN. Then, optimize structure of GaN:RE and investigate the changes of bond length and tetrahedral angle[10]. Finally, analysis of electronic structure of GaN:RE will be conducted.
2. Model
PHASE0 code [11] is performed to calculate electronic properties of pristine α-GaN and GaN:RE. This calculation uses Generalized Gradient Approximation (GGA)-Ultrasoft Pseudopotential at zero Kelvin. The cut-off wave function is 25 Ry and cut-off charge density is 225 Ry. Geometry optimization of a force $1.0^3$ Hartree/Bohr and the energy convergence is $1.0^3$ Hartree/Bohr. In unit-cell structure of pristine α-GaN, two atoms Ga are placed at the (0,0,0) and (2/3,1/3,1/2) and two atoms N at the (0,0,u) and (2/3, 1/3, u+1/2), which $u$ is internal parameter. The vector is $a_1=(a,0,0), a_2=(a/2,a^\sqrt{3}/2,0)$ and $a_3=(0,0,c)$, which $a$ and $c$ are lattice parameter[10]. For GaN:RE, the RE will be substituted in Ga site, see Figure 1. The RE will occupy cation site in the GaN. When Ga is substituted with RE, the configuration turns into Ga$_{(1-x)}$N$_x$RE$_x$ (1≤$x$≤0). In this calculation, $x$ is concentration of RE in GaN structure which $x=0.125$. Pristine α-GaN and GaN:RE will be performed in k-point mesh ($2^x2^x2^x$) of hexagonal lattice on Brillouin zone (BZ) GaN.

![Figure 1. Model of supercell GaN:RE in 16 atoms, which one atom Ga substituted with one atom RE. For example the RE is Tm. Ga atom is symbolized with pink color, N with blue color and Tm with green color.](image)

3. Result and Discussion
Optimization equilibrium geometry of the pristine α-GaN follows the procedure Stampfl et. al[12]. Lattice parameter of pristine α-GaN is found as $a=3.1438$ Å and $c= 5.1254$Å . This results is ~2% smaller than experimental data and from theoretical calculation [10][13]. Internal parameter of $u=0.3768$ and ratio of $c/a=1.6303$ have slightly changed. The bond length of Ga-N is 1.9266 Å and the tetrahedral angle of N-Ga-N is 109.16°, this tetrahedral angle is smaller from ideal wurtzite structure [14]. In general, the result of equilibrium lattice constant is slightly changed with experimental data and another theoretical calculations.

Figure 2 shows electronic properties of pristine α-GaN the band structure and total density of states (DOS). Outer orbital electron of 2p N and 3d Ga effect on lower valence band in the energy range between -12.5 eV until -15 eV. The band structure shows direct band gap, $E_g$, as it has detected 2.58 eV. This is 1 eV lower than experimental data. GGA calculation in electronic structure of GaN is still underestimated. Direct band occurs because of the minimum point of conduction band, $C_b$, and maximum point of valence band, $V_a$, are parallel in Γ-point.

The substitution of one atom RE to α-GaN made the structure changes. RE atoms is grater than Ga atom, this is effected to the bond length and tetrahedral angle [15]. Geometry optimization of GaN:RE was also implemented to get convergence of total energy. Four atoms of Nitrogen are the nearest neighboring atoms of RE with one atom bonded above and three atoms bonded in the lower. Table 1 shows the bond length and tetrahedral angle in several RE doped. The bond length of RE-N is varies
with the closest bond is Ga-Tm (2.1277Å) and the longest is Ga-Pr (2.235Å). The bond length increases 12% from Ga-N, this is shorter from another calculation [6][10][16]. The bond length of RE-N impacts to the tetrahedral angle N-RE-N. This occurs because Tm has high density with electron 4f\textsuperscript{13} while Pr has 4f\textsuperscript{3}.

**Figure 2.** Electronic properties of pristine at 16 atoms supercell the band structure (left) and Density of States (DOS) (right). The position of Fermi energy, E\textsubscript{F}, is denoted by vertical dotted line, which set to be 0.0 eV.

The band structure and DOS of GaN:RE are shown in the Fig. 3. Impurity energy is formed between conduction band (C\textsubscript{b}) and valence band (V\textsubscript{b}) of host material. On the band structure, the position energy level of C\textsubscript{b} and V\textsubscript{b} is decreases. The distance from minimum point C\textsubscript{b} to maximum impurity energy level of GaN:Eu is 0.95 eV. The conduction level decreased with minimum point 1.24 eV. Maximum point of V\textsubscript{b} is changed from Γ to K. The distance of minimum impurity energy level between V\textsubscript{b} is 1.22 eV. It is predicted as the effect of Eu to crystal lattice where hexagonal lattice of BZ changed.

**Table 1.** Geometries optimization of GaN:RE (RE=Pr, Eu, Gd, Er, Tm). RE-N\textsuperscript{***} is three bonds and RE-N\textsuperscript{*} is one bond.

| Supercell | RE-N\textsuperscript{***} (Å) | RE-N\textsuperscript{*} (Å) | N-RE-N angles(°) |
|-----------|------------------|-----------------|-----------------|
| GaN:Pr    | 2.1672           | 2.2350          | 113.28          |
| GaN:Eu    | 2.1427           | 2.2009          | 112.92          |
| GaN:Gd    | 2.1346           | 2.1903          | 112.70          |
| GaN:Er    | 2.1306           | 2.1887          | 111.93          |
| GaN:Tm    | 2.1277           | 2.1278          | 111.50          |
Figure 3. The band structure (left) and DOS (right) of (a) GaN:Eu, (b) GaN:Er and (c) GaN:Tm. All supercell formed 16 atoms. The position of Fermi energy, $E_f$, is denoted by vertical line, which has been set to be 0.0(eV).
The distance from Cb to maximum impurity of Gan:Er is 1.69 eV and GaN:Tm is 1.91 eV. The separation distances vary affecting to electron-hole excitation. It will produce different wavelength, three of them has red, green and blue colors [6][7]. Maximum valence band of GaN:Er and GaN:Tm are changed to M-point. The total energy DOS of the impurity energy RE has shown an increase then decrease. It shows the total DOS of GaN:Er (150 states/eV) is larger than GaN:Eu (100 states/eV) or GaN:Tm (120 states/eV). Impurity energy of RE in GaN has its own characteristics [17][18]. The energy level of Cb, Vb and impurity energy 4f are varied to host material for each RE doped. 4f electron of RE heavily influence to the band gap of host materials. Hybrid-DFT calculation is needed study in more details [17][18].

Summary
In this calculation, pristine α-GaN has direct band gap $E_g = 2.58$ eV. The lattice constant has changed 24% from the experimental data. When RE atoms substitute Ga, impurity energy has detected between conduction band and valence band. This affects the process of excite from RE to host materials. The energy level of conduction, valence and impurity RE have unique characteristics. Optical properties of GaN:RE can be predicted and can be used as optical devices.

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References
[1] B. Monemar, Phys. Rev. B 10 (1974) 676–681.
[2] S. Denbaars, D. Feezell, K. Kelchner, S. Pimputkar, C. Pan, C. Yen, S. Tanaka, Y. Zhao, N. Pfaff, R. Farrell, M. Iza, S. Keller, U. Mishra, J. Speck, S. Nakamura, Acta Materialia 61 (3) (2013) 945–951.
[3] S. Nakamura, T. Mukai, M. Senoh, Applied Physics Letters 64 (13) (1994) 1687–1689.
[4] V. Kachkanov, M. J. Wallace, G. van der Laan, S. S. Dhesi, S. A. Cavill, Y. Fujiwara, K. P. O’Donnell, Scientific Reports 2 (2012) 969.
[5] J. Heikenfeld, M. Garter, D. S. Lee, R. Birkhahn, A. J. Steckl, Applied Physics Letters 75 (9) (1999) 1189–1191.
[6] A. Steckl, J. Heikenfeld, D. Lee, M. Garter, Materials Science and Engineering: B 81 (13) (2001) 97 – 101.
[7] U. Hmmerich, J. Seo, C. Abernathy, A. Steckl, J. Zavada, Materials Science and Engineering: B 81 (13) (2001) 116-120.
[8] D. S. Lee, A. J. Steckl, Applied Physics Letters 82 (1) (2003) 55–57.
[9] A. J. Steckl, J. C. Heikenfeld, D. S. Lee, M. J. Garter, C. C. Baker, Y. Wang, R. Jone, IEEE Journal of Selected Topics in Quantum Electronics 8 (4) (2002) 749–766.
[10] K. C. Mishra, V. Eyert, P. C. Schmidt, Zeitschrift für Physikalische Chemie 221 (2009) 1663–1676.
[11] C. for Research on Innovative Simulation Software (CISS), the Institute of Industrial Science (IIS), the University of Tokyo, First-principles electronic structure calculation program phase/0.
[12] C. Stampfl, C. G. Van de Walle, Phys. Rev. B 59 (1999) 5521–5535.
[13] D. Andiwijayakusuma, M. Saito, A. Purqon, Journal of Physics: Conference Series 739 (1) (2016) 012027.
[14] X. L. CHEN, J. K. LIANG, Y. P. XU, T. XU, P. Z. JIANG, Y. D. YU, K. Q. LU, Modern Physics Letters B 13 (09n10) (1999) 285–290.
[15] S. Sanna, W. G. Schmidt, T. Frauenheim, U. Gerstmann, Phys. Rev. B 80 (2009) 104120.
[16] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, E. Yagi, Journal of Crystal Growth
237239, Part 2 (2002) 1027 – 1031.

[17] P. Dorenbos, E. van der Kolk, Applied Physics Letters 89 (6) (2006) 061122.
[18] G. Caroena, W. V. M. Machado, J. F. Justo, L. V. C. Assali, Applied Physics Letters 102 (6) (2013) 062101.