Computational Study of Electronic Structure Rare-Earth Doped Semiconductor III-V: GGA Approximation

Muhammad Y.H Widianto

Department of Informatics, Del Institute of Technology, Jl. Sisingamangaraja Laguboti Kab. Toba Samosir, Sumatera Utara, 2238, Indonesia

Abstract. Electronic structure of rare-earth doped semiconductor III-V have been investigated. Based on density functional theory GGA Approximation, the electronic structure of AlN and GaN are calculated in wurtzite structure. The direct band gap of pristine AlN and GaN has slightly changed from experimental results. Rare-earth atoms substitute group III elements and bonded with four N atoms. The bond length of RE-N have changed 14.5% from Al-N bond length. Impurity energy 4f of rare-earth has found between the conduction band and valence band. By this, the 4f energy can explain the luminescence process from rare-earth atoms to host materials. The band structure is expected to allow optical transition in IR-UV emission range. Rare-earth doped semiconductor III-V has high potential to be applied to lower energy of light emitting diodes and energy-saving devices.

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 has the direct transition with energy band gap ranging 1.9-6.2 eV for InN, GaN, and AlN[1][2]. Blue light-emitting devices 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]. Addition of impurities materials on the host material makes changes to the band’s energy. It is expected to be transformed from indirect bands into direct bands and highly efficient.

Rare-earth (RE) has unique properties, energy level 4f relative to valence band and conduction band of host materials[6]. Strong visible wavelength was explored when semiconductor III-V nitrides doped RE[7][8]. Energy of the f shell RE contributed to narrowing band energy, this is detected on RE doped which has high peaks spectral[9]. For example Eu atom has 6 electron in f shell, these produce red emission when doped in nitriles III-V[10]. Several RE doped AlN has been studied[11][12]. They found that AlN:Tm has energy band gap ranging of blue color[13]. Sharp peak energy was shown in the transition 5 D0 →7 F2 by RE ions doped which produce IR spectrum[14]. It is indicates that valence electron of RE excited to host materials. The defect RE ions made the crystal lattice change. By randomly placed RE on semiconductor III-V, the RE substitute position of group III elements[15]. Both of semiconductor III-V nitrides (AlN and GaN) doped RE seems to result in more energy-saving, temperature-stable and high brightness for visible-UV optical devices[16][17][18]. Basic understanding electronic structure of semiconductor III-V and doped RE are needed to explain the wide range energy band. In this paper, investigating the electronic properties of AlN and GaN doped...
RE was clarify based on DFT calculations. In Sec II. the computational model which is used. In Sec. III. the pristine of AlN and GaN was applied to findthe optimized of wurtzite structure. Analyzing the structure and electronic behavior of doped RE was also studied to understand the energy structure and the summary is in Sec. IV

2. Computational
PHASE0 is used to calculate electronic structure of pristine semiconductor III-V[19]. GGA Approximation was applied for exchange-correlation energy, Exc, to give rather accurate result for the systems[20]. 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 are generate 2 × 2 × 2 mesh generation for geometry optimization. Convergence of total energy is carefully examined to the cut-off energy and k-point sampling. Both of semiconductor III-V nitrides (AIN and GaN) are modeled in wurtzite structure 32 atoms (Fig. 1), the most stable in bulk structure. First, optimization of unit cell wurtzite structures are performed with four atoms per hexagonal unit cell. Group III elements are placed on (0,0,0) and (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 a=(a,0,0), b=(0.5a, 0.866a, 0), and c=(0,0,c), which a and c are lattice parameter of wurtzite structure[21]. These parameters are related by (c/a)2 = 1/u = 8/3. The composition RE on AlN structure written as Al(1−x)RExN (0 ≤ x ≤ 1), x is the RE dopant concentration. The independent parameters V, c, a, and u should be optimized as one by [22][27]

3. Result and Discussion
The stable structure of pristine AlN (GaN) in wurtzite structure have to be determined. The difference in the radius of Al and Ga make the lattice parameters must be optimized to get equilibrium, Al have smaller radius than Ga. Fig. 1 shows the lattice parameters a and c of AlN (GaN). The equilibrium point is slightly different, this is due to the difference of bond length Al-N and Ga-N. Lattice parameters of a AlN is smaller than GaN with the ratio establish (AlN:GaN =3.13:3.14). The difference of parameters ratio c/a AIN (GaN) from experimental results and this calculation is 1:0.9959 (1:0.9996)[16][10]. The distance of bond length Al-N and tetrahedral angle N-Al-N ease the understanding whether the hexagonal structure can be doped. π bond, single bond length of Al-N, and σ bonds, three bond lengths Al-N, are detected 1.9275 Å and 1.9011 Å. π and σ bonds Ga-N also calculated with ratio 3:2.985. The comparison of tetrahedral angle N-Al-N:Ga-N is 0.992:1, that is slightly narrow angle of ideal tetrahedral [27]. By using the calculation of GGA approximation, the lattice parameter a, c, u, bond length and tetrahedral angles of AlN (GaN) are slightly changed from experimental result[22]. This shows that the wurtzite structure of AlN (GaN) is stable.

| Supercell | π bond (Å) | σ bonds (Å) | Tetrahedral angle N-RE-N (°) |
|-----------|------------|-------------|-----------------------------|
| AlN:Pr    | 2.2631     | 2.1577      | 112.864                     |
| AlN:Eu    | 2.2233     | 2.1313      | 112.066                     |
| AlN:Ho    | 2.2094     | 2.1258      | 111.399                     |
| AlN:Er    | 2.2071     | 2.1223      | 110.877                     |
| AlN:Tm    | 2.2070     | 2.1182      | 110.021                     |

A small concentration (6.25%) of RE is given into semiconductor III-V wurtzite structure. The composition change according to the amount of mixed concentration, as a concentration
Al_{0.9375}\text{RE}_{0.0625}N (x = 0.0625). RE has a tendency to fill in the void of cation site replacing Al (Ga). RE atoms bound four N by pushing and substituting Al (Ga) in the tetrahedral structure. This made neighbor of atomic position hexagonal structure changes. Another study shown that Eu substitutionally occupied Al sites inside AlN lattice[23]. Table 1 shows the bond length RE-N and tetrahedral angle N-RE-N which RE = Pr, Eu, Ho, Er and Tm. The bond lengths and tetrahedral angle get larger when the number of 4fn electrons are small, that also happened to tetrahedral angles. The tendency RE-N have a shorter bond length with three bonds length nitrogen, σ bonds, compared to π bond. Another calculation Er-N bond length has ratio 1.015:1 (π bond) and 1.03:1 (σ bonds) with this work, which elongate to about 14.5% and 20% compared with bulk.

![Figure 1](image1.png)  
*Figure 1.* The method to find equilibrium geometry of wurtzite structure followed by [22]. Optimization of lattice parameters $a$ and $c$ of AlN and GaN until it reachs the equilibrium points with the lowest total energy (Ha).

![Figure 2](image2.png)  
*Figure 2.* The DOS of pristine AlN, AlN:Eu and AlN:Er, which composition Al_{1-x}RE_xN, (x = 0.0625). The position of Fermi energy, $E_f$, is denoted by doted vertical line, which has been set to be 0.0(eV).

In this section, study of electronic structure pristine AlN and AlN:RE is presented. Energy from RE affect the electronic structures of host materials. It may be used to determine the narrowing band gaps near the IR-visible light. The density of states (DOS) for pristine-AlN, AlN:Pr, AlN:Eu and AlN:Er are shown in Fig. 2. The fermi energy, $E_f$, was set to be 0.0 eV for convenience, denoted by dotted. In this calculations the $E_f = 0.3253$ eV. The highest occupied band energy (vbm) of AlN is detected
0.251 eV, the electrons fill the lowest energy level. Energy transfer is obtained when the excitation of the impurity becomes unoccupied, potentially use 4f energy. Band gap energy for pristine AlN shows 4.16 eV, it is smaller 33.3% than experimental result[22]. It also appears to pristine GaN that have wide band gap 19.38% smaller than experimental result[21]. Band structure also found in direct band gap obtained with CBM and VBM lies on Ω − Γ points, this calculation does not show in this section. It is because DFT calculation of GGA approximation underestimate. Calculation with Hubbard U provides accurate results by considering Coulomb interaction

A sharp peak was found around fermi energy. This ascribed to the 4f energy and detected in the AlN:Pr, AlN:Eu and AlN:Er as shown in Fig. 3. In the trivalent RE ions, energy level calculations is possible to simulate emission and absorption spectra[26]. AlN doped Eu3+ have emission peak intensity (5D0 → 7 F2), this correspond to the energy of the exciton bound on the host materials. The difference energy below CBM and top of 4f impurity energy, ∆Eci, of AlN:Pr, AlN:Eu, and AlN:Er are 1.09 eV, 2.18 eV and 3.02 eV respectively. The difference energy from minimum impurity energy and VBM, ∆Eiv, sequentially 2.01 eV, 1.20 eV, and 0.52 eV for AlN:Pr, AlN:Eu, and AlN:Er. For replacement of Al by RE is due to shift of the conduction band and valence band. 4f energy shift approach to the valence band when the electron valence 4fn is large. The locations of Eu 4f and 5d energy level lie within the band gap AlN:Eu, this can be assumed to verified by analysis Eu-doped spectra[23].

4. Conclusion

Investigation of semiconductor III-V pristine AlN (GaN) using DFT GGA Approximation was studied. Wurtzite structure of AlN (GaN) is stable structure although doping with RE in the small concentration. The atomic force relaxation surrounding RE materials makes the tetrahedral and bond length of RE-N elongated. Impurity energy 4f RE influence energy band and shift to lower energy region. The impurity level provides understanding the luminescence properties of rare-earth doped AlN and potentially to be applied to LED devices. The binding energy trivalent and divalent of RE relate the level energy position to determine luminescence and electronics of AlN:RE. This approximation affects to valence and conduction band of host materials. The binding energy RE to host materials is discussed in the future

Acknowledgments

This work was supported by GRID LIPI High Performance Computing for numerical calculations.

References

[1] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, Journal of Applied Physics 89, 5815–5875 (2001).
[2] I. Vurgaftman and J. R. Meyer, Journal of Applied Physics 94, 3675–3696 (2003).
[3] S. Nakamura, T. Mukai, and M. Senoh, Applied Physics Letters 64, 1687–1689 (1994).
[4] P. Fischer, J. Christen, and S. Nakamura, Japanese Journal of Applied Physics 39, p. L129 (2000).
[5] C. H. Park, C. Byoung-Ho, L. Keun-Ho, and C. K. J., Phys. Rev. B 49, 4485–4493 (1994).
[6] P. Dorenbos and E. van der Kolk, Applied Physics Letters 89, p. 061122 (2006).
[7] A. J. Steckl, J. C. Heikenfeld, D.-S. Lee, M. J. Garter, C. C. Baker, Y. Wang, and R. Jone, IEEE Journal of Selected Topics in Quantum Electronics 8, 749–766 (2002).
[8] D. S. Lee and A. J. Steckl, Applied Physics Letters 82, 55–57 (2003).
[9] V. Kumar, A. F. Khan, and S. Chawla, Journal of Physics D: Applied Physics 46, p. 365101 (2013).
[10] S. Goumri-Said and M. B. Kanoun, Journal of Physics D: Applied Physics 41, p. 035004 (2008).
[11] A. Wieg, Y. Kodera, Z. Wang, C. Dames, and J. Garay, Acta Materialia 86, 148 – 156 (2015).
[12] K. Gurumurugan, H. Chen, G. R. Harp, W. M. Jadwisienzak, and H. J. Lozykowski, Applied Physics Letters 74, 3008–3010 (1999).
[13] S. Petit, R. Jones, M. J. Shaw, P. R. Briddon, B. Hourahine, and T. Frauenheim, Phys. Rev. B 72, p. 073205 (2005).
[14] A. R. Zanatta, Journal of Physics D: Applied Physics 42, p. 025109 (2009).
[15] S. Sanna, W. G. Schmidt, T. Frauenheim, and U. Gerstmann, Phys. Rev. B 80, p. 104120 (2009).
[16] S. Wang, X. Wang, J. Li, Y. Jia, and F. Wang, Modern Physics Letters B 29, p. 1550114 (2015).
[17] A. Steckl, J. Heikenfeld, D. Lee, and M. Garter, Materials Science and Engineering: B 81, 97 – 101 (2001).
[18] J. Heikenfeld, M. Garter, D. S. Lee, R. Birkhahn, and A. J. Steckl, Applied Physics Letters 75, 1189–1191 (1999).
[19] C. for Research on Innovative Simulation Software (CISS), the Institute of Industrial Science (IIS), and the University of Tokyo, (2014).
[20] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865–3868 (1996).
[21] D. Andiwijayakusuma, M. Saito, and A. Purqon, Journal of Physics: Conference Series 739, p. 012027 (2016).
[22] C. Stampfl and C. G. Van de Walle, Phys. Rev. B 59, 5521–5535 (1999).
[23] L.-J. Yin, G.-Z. Chen, Z.-Y. Zhou, X. Jian, B. Xu, J.-H. He, H. Tang, C.-H. Luan, X. Xu, J. R. van Ommen, and H. T. (Bert) Hintzen, Journal of the American Ceramic Society 98, 3897–3904 (2015).
[24] K. C. Mishra, V. Eyert, and P. C. Schmidt, Zeitschrift fr Physikalische Chemie 221, 1663–1676 (2009).
[25] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, and E. Yagi, Journal of Crystal Growth 237239, Part 2, 1027 – 1031 (2002).
[26] P. Peijzel, A. Meijerink, R. Wegh, M. Reid, and G. Burdick, Journal of Solid State Chemistry 178, 448 – 453 (2005).
[27] M. Widianto, A. Purqon, Journal of Physics: Conference Series 877 (1) (2017) 012027.