Computational predictions of the new Gallium nitride nanoporous structures

Le Thi Hong Lien¹, Vu Ngoc Tuoc¹, Do Thi Duong² and Nguyen Thu Huyen²

¹Institute of Engineering Physics, Hanoi University of Science and Technology, 1 Dai Co Viet Road, Hanoi, Viet Nam

²Hong Duc University, 307 Le Lai, ThanhHoa city, Viet Nam

E-mail: lien.lethihong@hust.edu.vn

Abstract. Nanoporous structural prediction is emerging area of research because of their advantages for a wide range of materials science and technology applications in opto-electronics, environment, sensors, shape-selective and bio-catalysis, to name just a few. We propose a computationally and technically feasible approach for predicting Gallium nitride nanoporous structures with hollows at the nano scale. The designed porous structures are studied with computations using the density functional tight binding (DFTB) and conventional density functional theory methods, revealing a variety of promising mechanical and electronic properties, which can potentially find future realistic applications. Their stability is discussed by means of the free energy computed within the lattice-dynamics approach. Our calculations also indicate that all the reported hollow structures are wide band gap semiconductors in the same fashion with their parent's bulk stable phase. The electronic band structures of these nanoporous structures are finally examined in detail.

Keyword: Gallium nitride, nanoporous; Structure prediction; DFTB

1. Introduction

Today, due to the advancement of technology, one can growth the material in layers or even in sub-layer with a desired composition. And moreover, it is expected to be able to manipulate the layers of materials in the desired positions. This opens the door to the creation of porous structures with special shapes.

So far, nanoporous materials have quickly become an important research direction [1, 2]. These nanomaterials are promising for sustainable applications, such as catalysts, gas separation, water purification, and batteries. Gallium nitride equipments is the optimal choice for many emerging power semiconductor applications and rapidly replaces existing silicon technology, providing opportunities for explosive growth over the next decade, including switching conversion in smart grid systems, renewable energy systems, RF radio frequencies), power supply modules for motors/cars, and satellite communications systems, radar technology and space electronics. In the field of semiconductor optics, Gallium nitride GaN [3, 4, 5] is increasingly used in LEDs, laser diodes and optical converters because of its stronger emission characteristics than Si, SiC, GaAs and GaP. AlGaN combined with GaN [6], is used in the semiconductor optical is designed for applications that ultraviolet light brightness extreme operating at wavelengths <400 nm, for example, Green, UV and LED white.

In this paper, we propose a plan for the design of nanoporous structures. Our approach depends on the arrangement of the hexagonal hollow size into the block GaN, keeping the chemical composition unchanged.

2. Computational details
2.1. Theoretical structure prediction approach

In this section, we will briefly introduce the theory of predictive structures we perform. The approach here is top to bottom. From a bulk super cell of GaN, we have created hexagonal holes, from the orthogonal system. This structure will be optimized to get the primitive cells. Then, the structure is run to recover to get the final structure (see Figure 1). The nanostructures reported here are characterized by their walls and their hollow dimensions. The hexagonal hollow size, \( k \), is measured in cubic hexagonal size units. Hollow walls are defined as the thickness between the voids, which may be walls (SW), two walls (DW), three walls (3W) and four walls (4W). In each of the structures of the wall we create different porous structures for study and evaluation. In each of them, the structure of the wall we create a different gap size structures to study and evaluate. Thus, we construct each corresponding structure in the form \( nW-k \) where \( n \) is the number of walls, \( k \) is the hexagonal hollow size. For example, a structure called DW-3 would have will have hollows of size 3 which are spaced by two walls of hexagonal blocks. To illustrate, the series is shown in Figures 1, 2, 3, 4, 5.

![Figure 1. Single-walled structures were investigated respectively as SW-2, Sw-3, ..., SW-8.](image1)

![Figure 2. Double-walled structures were investigated respectively as DW-2, DW-3, ..., DW-8.](image2)
Figure 3. Three-walled structures were investigated respectively as 3W-2, 3W-3,..., 4W-6.

Figure 4. Four-walled structures were investigated respectively as 4W-2, 4W-3,..., 4W-7.

Figure 5. Four structures with cavity radii but the number of walls varies from 1 to 4.

2.2. Density functional based tight binding method
Density Functional based tight binding (DFTB) [7,8] is an approximate approach density functional theory (DFT) that extends the computational scope of DFT tools because they have roughly equivalent levels of accuracy but have computational time faster than the exponent DFT. Thus, it allows study the electronic structure of large systems that cannot be exploited with traditional DFT. However, DFTB requires pre-set parameter files for all pairs of atoms in the compound.

Our calculations are done in a tight-fitting approach (DFTB) [9-12]. This method is based on the second-order extension of the spin-based Kohn-Sham total energy function involving a
defined reference charge and the magnetization density. You can find more details on DFTB + in [13,14] and the references in it. In our calculation, the parameter and its conversion properties have been successfully applied in some previous DFTB projects [15, 16]. For exchange-correlation energy we use the functions of Perdew-Burke-Ernzerhof (PBE) [17] and Heyd-Scuseria-Ernzerhof (HSE06) [18].

3. Results and discussions

3.1. Phase stability

For estimation nanoporous phase’s stability, we first calculated the total binding energy per Zn-O pair vs. volume for a series of uniformly strains around the relaxed lattice volume. Then the bulk modulus (BM) are obtained by nonlinearly fitting above data series to the third order Birch-Murnaghan equation of states (EOS) as performed in Ref. [19, 20]. The results are presented in Figure 6 as well as listed in the Table of characteristics. It should be noted that, during the optimization process, all the designed nanoporous phases are found to be energetically stable and therefore could survive without structural collapse, showing that these phases are physically relevant and might actually be nano-lattice porous phases for GaN. Also these all are suffered from surface relaxation due to the dangling bonds exposed at the internal hollow surface. The portion dangling bonds [21, 22, 23, 24] can be examined by considering the average coordination number (see Table of characteristics), which in some sense reflect the surface-to-volume ratio. For all series, this parameter is below four, which is the typical value of wurtzite coordination number and are varying with different hollow and wall sizes as decreasing while the hollow radius increase (see more in Tables).

| Structures     | GaN-Hex2-SW | GaN-Hex3-SW | GaN-Hex4-SW | GaN-Hex5-SW | GaN-Hex6-SW | GaN-Hex7-SW | GaN-Hex8-SW |
|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Mass Density (g cm⁻³) | 4.692       | 3.544       | 2.787       | 2.301       | 1.957       | 1.288       | 1.505       |
| Volume/atom (Å³/atom) | 14.817      | 19.618      | 24.941      | 30.207      | 35.516      | 53.985      | 46.182      |
| Part. density (10²³ cm⁻³) | 36.675      | 60.510      | 84.401      | 108.331     | 132.282     | 156.185     | 180.217     |
| Coord. Number      | 0.00        | 3.00        | 0.00        | 3.00        | 0.00        | 3.00        | 0.00        |
| Crystall structure | Hex         | hex         | hex         | hex         | hex         | hex         | hex         |
| Symmetry groups    | P31M (C3V-2)| P31M (C3V-2)| P31M (C3V-2)| P31M (C3V-2)| P31M (C3V-2)| P31M (C3V-2)| P31M (C3V-2)|
| Unit cell (Atoms)  | 36          | 60          | 84          | 108         | 132         | 156         | 180         |
| Lattice param. Å (a-c) | 10.917927  | 16.246624   | 21.596548   | 26.944416   | 32.294316   | 37.644865   | 42.994103   |
| Aver.bond Å: Ga-Ga:Ga-N | 5.167124   | 5.196454    | 5.186669    | 5.189022    | 5.190745    | 5.191877    | 5.192761    |
| Aver.Angle Ga-N-Ga/N-Ga-N | 112.03     | 114.39      | 114.25      | 114.58      | 114.79      | 107.79      | 115.04      |
| Band gap eV       | 3.4014      | 3.6735      | 3.8912      | 3.8640      | 3.8368      | 3.8096      | 3.7824      |
| UC Connolly sur. area Å² | 91.98      | 193.43      | 299.91      | 404.31      | 508.85      | 613.33      | 717.80      |
Table 1. Calculated characteristics of all studied phase and most common phase of GaN–SW.

| Structures | GaN-hex-DW221 | GaN-hex-DW331 | GaN-hex-DW441 | GaN-hex-DW551 | GaN-hex-DW661 | GaN-hex-DW771 | GaN-hex-DW881 |
|------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Mass Density (g/cm³) | 6.066 | 4.786 | 3.882 | 3.246 | 2.783 | 2.433 | 2.141 |
| Volume/at (Å³/at) | 11.460 | 14.525 | 17.910 | 21.419 | 24.980 | 28.568 | 32.468 |
| Part. density (10²³ cm⁻³) | 46.873 | 82.688 | 118.558 | 154.467 | 190.400 | 226.350 | 262.308 |
| Coord. Number | 3.87 | 3.94 | 3.24 | 3.18 | 3.15 | 3.12 | 3.14 |
| Crystall structure | Hex | Hex | Hex | Hex | Hex | Hex |
| Symmetry groups | P31M (C3V-2) | P31M (C3V-2) | P31M (C3V-2) | P31M (C3V-2) | P31M (C3V-2) | P31M (C3V-2) |
| Unit cell (atoms) | 46 | 82 | 118 | 154 | 190 | 226 | 262 |
| Lattice param. Å (a-c) | 10.862025 | 5.159381 | 16.318867 | 5.164204 | 21.73099 | 5.169024 | 32.559 | 5.169904 | 37.978984 | 5.170486 | 43.384599 | 5.170661 |
| Aver. Bond Å: Ga-Ga; Ga-N | 1.912 | 2.927 | 1.894 | 1.884 | 1.878 | 1.874 | 1.872 | 2.923 | 1.876 |
| Average angle Ga-N-Ga/N-Ga-N | 109.69 | 110.56 | 111.39 | 111.16 | 112.12 | 11.52 | 112.55 | 111.76 | 112.84 | 111.93 | 113.05 | 111.52 | 113.48 |
| Band gap eV | 2.0953 | 3.5103 | 3.4558 | 3.4558 | 3.4558 | 3.4558 | 3.4831 | 3.4831 |
| UC Connolly surf. area Å² | 9.84 | 143.78 | 249.09 | 355.29 | 461.39 | 567.57 | 637.46 |
| UC Pore Volume Å³ | 524.19 | 945.56 | 1366.59 | 1784.59 | 2203.95 | 2623.78 | 3045.44 |

Table 2. Calculated characteristics of all studied phase and most common phase of GaN-DW.

| Structures | GaN-Hex2-3W331 | GaN-Hex3-3W441 | GaN-Hex4-3W551 | GaN-Hex5-3W661 | GaN-Hex6-3W771 | GaN-Hex7-3W881 |
|------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Mass Density (g/cm³) | 5.712 | 4.735 | 4.052 | 3.514 | 3.100 | 2.771 |
| Volume/at (Å³/at) | 12.171 | 14.682 | 17.157 | 19.784 | 22.426 | 25.084 |
| Part. density (10²³ cm⁻³) | 96.822 | 144.681 | 192.583 | 240.505 | 288.446 | 336.399 |
| Coord. Number Ga-Ga; Ga-N | 0.50 | 1.22 | 3.67 | 0.00 | 3.56 | 3.50 | 3.46 | 0.00 | 3.46 |
| Crystall structure | Hex | Hex | Hex | Hex | Hex | Hex |
Table 3. Calculated characteristics of all studied phase and most common phase of GaN-3W.

| Structures                  | GaN-hex12-4W331 | GaN-hex23-4W441 | GaN-hex34-4W551 | GaN-hex45-4W661 | GaN-hex56-4W771 | GaN-hex67-4W881 |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mass Density (g cm⁻³)       | 6.241           | 5.485           | 4.975           | 4.140           | 3.733           | 3.353           |
| Volume at (∅/at)            | 11.139          | 12.675          | 13.937          | 16.792          | 18.623          | 20.731          |
| Part. density (10²³ cm⁻³)  | 106.898         | 166.789         | 226.716         | 286.596         | 346.537         | 406.482         |
| Coord. Number               | 0.00            | 0.29            | 1.37            | 0.48            | 0.00            | 0.02            |
| Cr. structure               | hex             | hex             | hex             | hex             | hex             | hex             |
| Symmetry groups             | P31M (C3V-2)    | P31M (C3V-2)    | P31M (C3V-2)    | P31M (C3V-2)    | P31M (C3V-2)    | P31M (C3V-2)    |
| Unit cell (atoms)           | 106             | 166             | 226             | 286             | 346             | 406             |
| Lattice param. Å (a-c)      | 16.260907       | 21.701118       | 27.150467       | 32.598009       | 37.966864       | 43.392612       |
| Aver. bond Å Ga-Ga; Ga-N    | 1.917           | 2.292           | 2.863           | 2.917           | 1.902           | 2.928           |
| Average angle Ga-N-Ga/N-Ga-N| 109.56          | 109.69          | 109.41          | 110.17          | 110.63          | 110.73          |
| Band gap eV                 | 2.3130          | 3.7552          | 3.6191          | 3.6191          | 3.6191          | 3.6191          |
| UC Connolly surf. area Å²  | 9.58            | 142.67          | 238.13          | 361.67          | 460.89          | 567.21          |
| UC Pore Volume Å³           | 1177.93         | 1860.59         | 2441.78         | 3260.33         | 3905.75         | 4586.73         |

Table 4. Calculated characteristics of all studied phase and most common phase of GaN-4W.

3.2. Electronics properties
In order to determine would the newly designed GaN nanoporous phases, if synthesized, possess novel electronic properties, we firstly explore their band structures. Figure 6 shows the calculated of nanoporous phase’s band gap vs. their hollow size. It should be noted that they all are below the GaN wurtzite value [25] (~ 4.16eV within the DFTB+ parametrization used this work). Noted that within the used scheme, DFTB+ calculation had overestimated the GaN-w band gap, which is 3.4 eV from the room temperature experimental measurements about 20%. The gaps vary from 3.1 to 4.0 eV among the nanoporous series with different wall thickness denote by different color and symbol in Fig.5. Further, our results show that all nanoporous series are still wide band gap (WBG) semiconductors with a direct gap at the Gamma point. On the other hand, we observe general trend that the gap reduced with the increasing hollow radius then approaching to a certain saturated value at the large radius for each series. The reason is following the expected behavior of the quantum confinement effect. Also there are some evidence of the surface effect observed for the smallest cage’s radius structure for each series below the radius of 7Å, that causes the band gap is lowering due to the in-gap position of the surface states. This effect is more visible for the thinner series, i.e. SW and DW and less visible for the thick one as 3W and 4W. More over while the SW and DW series are separated each from other, the 3W and 4W series are very close. This might shows a tendency that the thicker series would approach to a certain convergence of saturation behavior, which helps our calculation prediction for the larger wall thickness. Overall, our result shows that the nanoporous phase band gap is an important parameter which could be turned due to their dependence to hollow size and wall thickness.
Our calculated bulk modulus (BM) are showing in Figure 7 and also listed at the Table of Characteristics, which indicates that for all series, while hollow size increases, the BM first falls rapidly then saturates at certain large hollow size. Also the thicker wall, i.e. 3W or 4W are more stable then the thinner with respect to same hollow radius as expected.

![Bulk modulus vs. hollow cage radius.](image)

**Figure 7.** Bulk modulus vs. hollow cage radius.

In order to estimate the relative strength of these nanoporous phases, we have made a figure, that draw the same data of BM but with respect to the phase’s porosity value called hollow-to-bulk density ratio in Figure 8. It is obviously that by increasing the hollow effective radius (denote by an arrow at the right corner) which equivalent to the increasing of phase’s porosity all the BM first fall rapidly then approaching to the linearly scaling line, i.e. thin 1:1 black line in the plot, called the strength-to-density scaling line. Furthermore, the series with thicker wall (larger than three layers) as 3W and 4W, become very close each other with respect to the same porosity (see lines in Figure 8). Therefore, we can make an assumption that although the BM values are separated for each series with respected to the hollow size (see Figure 7). However, they are very closed and even converged (for wall over the three layers) with respect to the phase’s porosity (see Figure 8). This is very important point for the applications. For example, our rule give a flexibility to choose between the desire BM value with corresponding wall thickness and how closer one can come to the of strength-to-density scaling line, which means closer to the bulk value of strength-to-density figure of merit.
4. Conclusion

These results show that changing the hollow size and the number of walls of the structure will change their physical and chemical properties for specific applications. This makes the nanomaterials more important. Nano-porous structures, due to their ability to interact with ions or both atoms and aggregates, make them especially useful in catalytic or membrane applications.

We believe that theoretical predictions from our simulation model can provide parameters for the design of nanoscale material models for computation. From our analyses of structure, electronics, and thermodynamic properties, it can be clearly shown that nanofunctions can actually describe nano-crystalline materials and low density. Due to the influence of the hole / wall size distribution on the properties of nanomaterials, an important parameter in practical fabrication applications is the gap-engineering.

Acknowledgments

This work was supported by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.01-2017.24.

References

[1] Meza L R, Das S, Greer J R 2014 Science 345 1322
[2] Mezaa L R, Zelhofer A J, Clarkeb N, Mateosa A J, Greer J R 2015 PNAS 112 11502-11507
[3] Bauer J, Schroer A, Schwaiger R and Kraft O 2016 Nat. Mater. 15 438
[4] Tian Y, Zhang Y, Wang T, Xin H L, Li H, and Gang O 2016 Nat. Mater. 15 654
[5] Xiong H, Sfeir M Y, and Gang O 2010 *Nano Lett.* **10** 4456
[6] Bauer J, Schroer A, Schwaiger R, and Kraft O 2016 *Nat. Mater.* **15** 438
[7] DFTB+ [Online http://www.dftb-plus.info/ http://www.dftb-plus.info/]
[8] Willander M 2014 *Pan Stanford*
[9] Elstner M, Porezag D, Jungnickel G, Elsner J, Frauenheim Th, Seifert G 1998 *Phys. Rev. B* **58** 7260
[10] Kohler C, Seifert G, and Frauenheim T 2005 *Chem. Phys.* **309** 23
[11] Aradi B, Hourahine B, and Frauenheim Th 2007 *J. Phys. Chem. A* **111** 5678
[12] Carrasco J, Illas F, and Bromley S T 2007 *Phys. Rev. Lett.* **99** 235502
[13] Wang Z L 2004 *J. Phys. Cond. Matt.* **16** R829
[14] Wang Z L and Song J 2006 *Science* **312** 242
[15] Moreira N H, Dolgonos G, Aradi B, da Rosa A L, Frauenheim Th 2009 *J. Chem. Theor. Comput.* **5** 605
[16] Tuoc V N 2010 *Comput. Mater. Sci.* **49** S161
[17] Perdew J P, Burke K, and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[18] Heyd J, Scuseria G E, and Ernzerhof M 2006 *J. Chem. Phys.* **124** 219906
[19] Vu Ngoc Tuoc, Tran Doan Huan, Nguyen Viet Minh, Nguyen Thi Thao 2016 *Journal of Physics: Conference Series* **726** 012022.
[20] Nguyen Thi Thao and Vu Ngoc Tuoc 2016 *VNU Journal of Science: Mathematics – Physics* **32** 1-10
[21] Vu Ngoc Tuoc, Tran Doan Huan, Nguyen Thi Thao 2017 *Physica B: Physics of Condensed Matter* [http://dx.doi.org/10.1016/j.physb.2017.03.003]
[22] Tuoc V N, Huan T D, and Lien L T H 2014 *IEEE Trans. Magn.* **50** 2400407
[23] Yong Y, Li X, Hao X, Cao J, and Li T 2014 *RSC Adv.* **4** 37333
[24] Vu Ngoc Tuoc, Tran Doan Huan, Nguyen Thi Thao and Le Manh Tuan 2016 *J. Appl. Phys.* **120** 142105
[25] Tuoc V N, Huan T D, and Lien L T H 2012 *Phys. Stat. Sol.* B **249** 1241
[26] Sponza L, Goniakowski J, and Noguera C 2015 *Phys. Rev.* B **91** 075126
[27] Zwijnenburg M A, Illas F, and Bromley S 2010 *Phys. Rev. Lett.* **104** 175503