Ab initio study of structural and electronic properties of (GaN)n/(AlN)n superlattices

L. Djoudi*a,b*, M. Merabet a,b, F. Dahmane b, M. Boucharef a, S. Benalia a,b, D. Rached a

aLaboratoire des Matériaux Magnétiques, Faculté des Sciences, Université Djillali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès (22000), Algeria
bUniversity of Tissemsilt, Institute of Science and Technology 38000, Algeria

E-mail: djoudilakhdar@yahoo.fr

Abstract. Structural and electronic properties of binary GaN and AlN compounds and their superlattices (SLs) (GaN)n/(AlN)n are investigated using the first-principles full potential linear muffin-tin orbitals method (FP-LMTO). The exchange-correlation potential is treated with the local density approximation of Perdew and Wang (LDA-PW). The ground-state properties are determined for the bulk materials GaN, AlN, and their superlattices (GaN)n/(AlN)n in cubic phase. The calculated structural properties of GaN and AlN compounds are in good agreement with available experimental and theoretical data. It is found that AlN exhibit an indirect fundamental band gap while that GaN and the superlattices (SLs) exhibit a direct fundamental band gap, which might make the superlattices (GaN)n/(AlN)n materials promising and useful for optoelectronic applications. The fundamental band gap decreases with increasing the number of monolayer.

1. Introduction

The study of semiconductor heterostructures, like quantum wells and superlattices, has resulted in an ever expanding and dynamic area of research over the past three decades. Semiconductor heterostructures are ultra-thin layered materials whose thicknesses are in the range of a few atomic layers. The presence of these ultrathin layers leads to the "quantum size effect" when the physical dimensions of the layers are comparable to the De Broglie wavelength of the charge carrier [1]. This new effect is of great interest both in fundamental physics and in devices applications [2]. Semiconductor superlattices consist of thin layers of alternating semiconductors typically 10-100 layers ranging from 10 to 500 Å in thickness. The constituent materials have different band gap and the conduction band edges for the two materials are not aligned; consequently, carriers experience a periodic potential along the growth axis, essentially forming a two-dimensional artificial crystal.

A superlattice is a periodic heterostructures formed by two types of semiconducting materials, one type that acts as a quantum well and the other acting a quantum barrier. The structure are grown by alternating the well and the barrier material such that the layers of well material are all of width \( L_w \) and the barrier layers are all of width \( L_b \). The superlattice is thus a periodic structure with period \( d = L_w + L_b \). The artificial periodicity created in superlattices...
can lead to the tailoring of certain material properties for applications in fields such as optoelectronics [3, 4]. The III–V superlattices which have wide band gaps having physical properties where that are very promising for the development of the optoelectronic devices in the visible and the ultraviolet regions of the electromagnetic spectrum with photon energies spread in a wide energy range [5]. Noteworthy, progress has been made during the past few years in the growth of III–V nitride material and devices. Due to the wide range of direct band gaps provided by nitride system. Band gap tuning is possible by forming alloys of the compounds with gaps of desired ranges [6]. However, understanding the basic properties of wide band-gap GaN and AlN and their superlattices, are currently of great academic and technological interest from the designing of novel materials to the fabrication of nanoelectronic and photonic devices [7].

The relevance of the materiel combination (GaN/AlN) is in combination of different band gap type and combination of very different direct band gap values (4.1 eV for AlN and 1.64 eV for GaN) [8, 9], special attention has to be paid to the GaN/AlN compounds, because the two binary compounds which are involved have common atom which is the nitride atom. Superlattices come predominately in two types. In the so-called “type-I” superlattices, where electrons and holes are confined to the same layers, is exemplified by the (GaP)n/(AlP)n and (CdTe)n/(ZnTe)n [10, 11]. In “type-II” superlattices, the electron and holes are confined to different layers, example of “type-II” superlattices composition is (BP)n/(BAs)n and (BeTe)n/(CdS)n [12, 13].

Knowing that, the III-V nitride system and their compounds have attracted much interest for years for this very reason. Having a much higher breakdown field, saturation velocity and thermal conductivity than GaAs, GaN offers great potential for high power devices [14]. Gallium nitride (GaN), aluminum nitride (AlN) and related materials are of considerable current interest because of their applications in light emitting devices operating in the visible and deep ultraviolet (UV) spectral regions [15-20]. In addition, AlN and GaN have a high melting point, a high thermal conductivity, and a large bulk modulus [21]. These properties, as well as the wide band gaps, are closely related to their strong (ionic and covalent) bonding. These materials can therefore be used for short wavelength light-emitting diodes (LED's) laser diodes, and optical detectors, as well as for high-temperature, high power, and high-frequency devices [22].

In this paper, we report first-principles study of the structural and electronic properties of bulk GaN, AlN and superlattices (GaN)n/(AlN)n (n number of monolayers; n = 1, 2 and 3) in the zinc-blend structure (B3), using the full-potential linear muffin-tin orbital (FP-LMTO) method, in the framework of the density functional theory (DFT) within the LDA. The organization of the article is as follows. The computational method we have adopted for the calculations is described in section 2. We present our results in section 3. Finally, conclusions are given in section 4.
2. Calculation Method

In the present study, the structural and electronic properties of binary GaN and AlN compounds and their \((\text{GaN})_n/(\text{AlN})_n\) superlattices are investigated using the first-principles full potential linear muffin-tin orbitals method (FP-LMTO) simulation program based on the density functional theory (DFT) within the local density approximation of Perdew and Wang (LDA-PW) [23]. In this theory, the quantum many-body problems of interacting electrons and nuclei can be mapped onto a system of one electron equations called Kohn–Sham equations [24, 25]. The space in the (FP-LMTO) method is divided into non-overlapping muffin-tin (MT) spheres centered at the atomic sites separated by an interstitial region (IR). In the IR regions, the basis set consists of plane waves. Inside the (MT) spheres, the basis sets is described by radial solutions of the one particle Schrodinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics. The exchange and correlation potential is treated by the local density approximation (LDA) [23]. The details of calculations are as follows: the charge density and the potential are represented inside the muffin-tin (MT) spheres by spherical harmonics up to \(l_{\text{max}} = 6\). The self-consistent calculations are considered to be converged when total energy of the system in stable within \(10^{-5}\) Ry. Accurate Brillouin integrations zone is performed using the tetrahedron method [26]. The corresponding integrating points over the irreducible Brillouin (IBZ) are 22 k-points for the bulk binary compounds (GaN and AlN), 64 k-points for SL(1,1) and 32 k-points for SL(2,2) and 98 k-points for SL(3,3). In order to achieve energy eigenvalues convergence, the wave functions in the interstitial regions were expanded in plane waves up to 270.9592 and 291.5794 Ry for GaN and AlN, respectively. For superlattices, the wave functions are expanded in plane waves up to approximately 222.6561, 222.6027 and 240.6854 Ry for SL (1,1), SL (2,2) and SL (3,3) respectively. The number of 12050 planes waves is used for both compounds GaN and AlN. For the superlattices, the number of plane waves is 16242, 32458 and 48690 for SL (1,1), SL (2,2) and SL (3,3) respectively. To avoid the overlap of atomic spheres the (MT) radius for each atomic position is taken to be different for each case.

3. Results and Discussions

3.1. Structural properties

The ground-state structural parameters have been obtained by minimizing the total energy with respect to the volume, by fitting this total energy versus the volume data on the non-linear Murnaghan equation of state [27]. Hence, first we computed the lattice parameter of the GaN and AlN in their cubic structure with the space group F-43m (no. 216). Geometry of (GaN)n/(AlN)n superlattice are shown in Fig. 1. Then, we studied the (GaN)n/(AlN)n superlattices where \(n\) is the number of monolayers the selected \(n\): 1, 2 and 3. The lattice mismatch for GaN/AlN superlattice is a 2.89% between its two constituent bulk semiconductors, so the lattice mismatch problem does not arise. In Table 1, we summarize the calculated lattice constants and the bulk module and its pressure derivative of binaries (GaN and AlN) and the superlattices (GaN)n/(AlN)n together with the available experimental and theoretical data. As can be seen, the obtained lattice constants for GaN and AlN are in reasonable agreement with the experimental data, for GaN is 0.88% greater and for AlN is 0.8% greater, than the experimental value, which ensures the reliability of the present first-principles computations. It is found out that the calculated bulk modulus for GaN is 12.86% less than the experimental value. The lattice parameter of (GaN)n/(AlN)n superlattices (n: 1, 2 and 3) has been found that \(a_1,1\) is equivalent to \(a_0(\text{GaN})+a_0(\text{AlN})/2\), \(a_2,2\) is about twice larger than \(a_1,1\) and \(a_3,3\) is threefold larger than \(a_1,1\). The lattice constant of (GaN)n/(AlN)n superlattices depending on \(n\) (the number of monolayers) is shown in Fig. 2. It is very clear from Fig. 2 that the lattice constant of (GaN)n/(AlN)n superlattices increase linearly with the number of monolayers increasing.
Figure 1. Geometry of (GaN)$_n$/(AlN)$_n$ superlattice ($n = 1, 2$ and $3$).

Figure 2. Lattice constant of (GaN)$_n$/(AlN)$_n$ superlattices as function of $n$ the number of monolayers.
Table 1. Calculated lattice parameter $a_0$, the bulk modulus $B_0$ and its pressure derivative $B'_0$ for zinc-blende GaN, AlN and the superlattices (GaN)$_n$(AlN)$_n$ ($n = 1, 2$ and 3) compounds at equilibrium volume compared to the available theoretical and experimental data.

|                | Present work | Experimental works | Other theoretical works |
|----------------|--------------|--------------------|-------------------------|
|                | $a_0$ (Å)    | $B_0$ (GPa)        | $B'_0$ (GPa)            | $a_0$ (Å)    | $B_0$ (GPa) | $B'_0$ (GPa) |
| GaN            | 4.570        | 165.562            | 3.8057                  | 4.49 [28]   | 4.46 [32]   | 3.2 [36]     |
|                |              |                    | 190 [31]                | 4.53 [29]   | 4.51 [33]   | 2.1 [37]     |
|                |              |                    |                         | 4.50 [30]   | 4.494 [8, 9] | 1.64 [8, 9] |
| AlN            | 4.405        | 182.03             | 3.835                   | 4.37 [28]   | 4.346 [34]  | 3.22 [35]    |
|                |              |                    |                         | -           | 206 [35]    | 3.32 [32]    |
|                |              |                    |                         | -           | 201 [8, 9]  | 3.19 [8, 9]  |
| (GaN)$_1$/ (AlN)$_1$ | 4.411        | 194.528            | 3.977                   | -           | -           | -            |
| (GaN)$_2$/ (AlN)$_2$ | 8.823        | 200.851            | 4.176                   | -           | -           | -            |
| (GaN)$_3$/ (AlN)$_3$ | 12.728       | 201.880            | 3.967                   | -           | -           | -            |

From Table 1, we noticed that the calculated bulk moduli for the (GaN)$_n$(AlN)$_n$ superlattices increase non-linearly with the number of monolayers increasing and a non-linear variation of the derivative of the bulk moduli for the (GaN)$_n$(AlN)$_n$ superlattices has been also observed.

3.2. Electronic properties

We have calculated the electronic band structure properties of GaN, AlN and (GaN)$_n$(AlN)$_n$ superlattices where $n$ is the number of monolayers the selected $n$: 1, 2 and 3 in the zinc-blende structure at this equilibrium lattice constants. We note that the good knowledge of electronic band structure in semiconductors provides valuable information as regarding their potential utility in fabricating electronic and optoelectronic devices. In table 2, we have listed the obtained direct and indirect band-gaps, at the high-symmetry point $\Gamma$ in the Brillouin zone, for the systems investigated and compared the results with available experimental and theoretical data. The results clearly show that the band gap are, on the whole, underestimated by about 54.69 % compared with experimental data for GaN, but are in good agreement with other theoretical data. The large difference in the calculated values of the band gaps as compared to the experimental values can be explained by the well-known fact that, in the electronic band structure calculations within DFT, LDA underestimates the energy gaps in semiconductors, we can see this in several papers that have already been published. The results show that GaN has a direct-gap with the minimum of conduction band at the $\Gamma$ point (Fig. 3. a); AlN has an indirect-gap with the minimum energy gap at the $X$ point (Fig. 3. b).

Table 2. Calculated direct and indirect band gaps for zinc-blende GaN, AlN and the superlattices (GaN)$_n$(AlN)$_n$ ($n = 1, 2$, and 3) compounds at equilibrium volume compared to the available theoretical and experimental data.

|                | Present work | Experimental works | Other theoretical works |
|----------------|--------------|--------------------|-------------------------|
|                | Eg (Direct) (eV) | Eg (Indirect) (eV) | Eg (Direct) (eV) | Eg (Indirect) (eV) | Eg (Direct) (eV) | Eg (Indirect) (eV) |
| GaN            | 1.43         | 4.46               | 3.2 [36]               | -               | 1.52 [32]        | 3.22 [32]          |
|                |              |                    |                         |                | 2.1 [37]         | 1.64 [8, 9]        |
|                |              |                    |                         |                |                 | 3.19 [8, 9]        |
| AlN            | 4.09         | 3.3752             | -                       | -               | 4.13 [35]        | 3.20 [8, 9]        |
| (GaN)$_1$/ (AlN)$_1$ | 3.1213       | 3.3302             | -                       | -               | 4.10 [8, 9]      | -                  |
| (GaN)$_2$/ (AlN)$_2$ | 3.0454       | 3.1209             | -                       | -               | -                | -                  |
| (GaN)$_3$/ (AlN)$_3$ | 3.0477       | 3.0067             | -                       | -               | -                | -                  |

The calculated band gap energies of (GaN)$_1$/ (AlN)$_1$, (GaN)$_2$/ (AlN)$_2$ and (GaN)$_3$/ (AlN)$_3$ along the higher symmetry directions of Brillouin zone are shown in (Fig. 4. a), (Fig. 4. b) and (Fig. 4. c)
respectively. From the results of the calculated band gap energies, we find that these materials have direct band gap for \( n = 1 \) and 2, which is of interest for optoelectronic devices, but for \( n = 3 \) this superlattice become have indirect band gap. It is important to note that the results found are automatically small, because we must not forget that the LDA method greatly underestimates the band gap in semiconductors, so we can predict that the direct band gap values for \((\text{GaN})_n/(\text{AlN})_n\) superlattices for \( n = 1, 2 \) and 3 are 6.8887, 6.7212 and 6.7262 eV, respectively. It is very clear from table 2 that the direct and indirect band-gaps decrease with the increasing of the \( n \) number of monolayers. We note that the difference in the band gaps of the \((\text{GaN})_n/(\text{AlN})_n\) superlattices and the end compounds is usually attributed to charge transfer, reflected in terms of the electronegativity difference of the mixing cations and anions.

![Figure 3 (a and b). Band structure along the symmetry lines of the Brillouin zone at the equilibrium lattice constant for GaN and AlN compounds. The position of the Fermi level is shown by horizontal solid line.](image)

To obtain a deeper insight into the electronic structure, we have also displayed in (Fig. 5. a) and (Fig. 5. b), the total and the partial atomic site-decomposed density of states (TDOS and PDOS) for GaN and AlN compounds, respectively and in (Fig. 6. a), (Fig. 6. b) and (Fig. 6. c) their \((\text{GaN})_n/(\text{AlN})_n\) superlattices \((n = 1, 2\) and 3) in order to analyze the contributions from the different states of Ga, Al and N atoms. The results shown in (Fig. 5. a) and (Fig. 5. b) shows that the upper valence bands from \(-19.4272\) to \(0.1727\) eV and from \(-19.4272\) to \(-1.2217\) eV for GaN and AlN, respectively, are governed by hybridization N-2s, Ga-4s and N-2p states for GaN and N-2s, N-2p and Al-3s states for AlN, in the two intervals (-19.4272 to 0.1727 eV for GaN) and (-19.4272 to -1.2217 eV for AlN) can be observed two structures for GaN and two structures for AlN. The first structure (from -19.4272 to -11.0272 eV for GaN and -19.4272 to -13.8217 eV for AlN) is due to the N-2s and with a small
Figure 4 (a, b and c). Band structure along the symmetry lines of the Brillouin zone at the equilibrium lattice constant for (GaN)$_n$/(AlN)$_n$ superlattices (n = 1, 2 and 3). The position of the Fermi level is shown by horizontal solid lines shown by horizontal solid line.
contribution from Ga-4s for GaN and is due to the N-2s and with a small contribution from Al-3s for AlN, the second structure (from -8.2272 to 0.1727 eV for GaN) and (from -8.2217 to -1.2217 eV for AlN) is due to the N-2p and with a small contribution from Ga-4s for GaN and to the N-2p and with a small contribution from Al-3s for AlN. The structure above the Fermi level is broad and extends up to 20 eV for both compounds. As in the two binary, the calculated total and partial densities of states of these superlattices show a resemblance with some small differences in details. We noticed that the contribution of different orbitals is proportional to the number of monolayer of the two components of the superlattice. The densities of states of the valence and conduction bands of the superlattice are characterized by three regions separated by gaps. Following these figures Fig. 6. a), Fig. 6. b) and Fig. 6. b), the first region, in the valence bands, for the three configurations is mainly due to the contribution of Ga-3d and N-2s states with a small contribution from Al-3s states. The second structure is due to the Al-3p and N-2p with a very small contribution from Al-3s. The third region in the conduction band the three superlattices have the same contribution in the total density of states. These contributions are formed by a hybridization of s, p and d states of the three atoms.

Figure 5 (a and b). Total and partial density of states (DOS) for GaN and AlN compounds.
Figure 6 (a, b and c). Total and partial density of states (DOS) for (GaN)_n/(AlN)_n superlattices (n = 1, 2 and 3).
4. Conclusion

The full potential linear muffin-tin orbitals method (FP-LMTO) approach based on the density functional theory (DFT), within the local density approximation of Perdew and Wang (LDA-PW) is utilized to investigate the structural and electronic properties of GaN and AlN compounds and their (GaN)n/(AlN)n superlattices. The calculated lattice parameter and bulk modulus of each binary compounds are in reasonable agreement with experimental values. From the calculated results, it is found that the lattice constant of (GaN)n/(AlN)n superlattices is depending on n the number of monolayers. The calculated band structure show that GaN has a direct-gap, AlN has an indirect gap and the (GaN)n/(AlN)n superlattices has a direct gap and decreases with increasing the number of monolayers also we noticed that, from n equals three the superlattice become have indirect band gap. Finally, one can point out that the direct gap character that the (GaN)n/(AlN)n superlattices exhibit is of great importance for the optical transitions and might be useful for the design of quantum well lasers and solar cell heterostructures. To the best of our knowledge, there is no publications available on the structural (a₀, B₀ and B₀') and electronic (band gaps) properties of for the studied superlattices are available to be compared with our theoretical results.

5. References

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