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New Buckled Structures of Bilayer GaN and their Properties.

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Abstract

New structures of bi-layer GaN are uncovered and studied using first-principles calculations. These structures are buckled and they are shown to be more stable than flat bilayer GaN. The electronic properties of these structures are studied. The changes with respect to the flat bilayer are shown to occur due to the p_z orbitals of N atoms, which dominate in the highest valence states. Interestingly, these structures undergo an indirect-to-direct band gap transition under compressive strain.

1. Introduction

In the last decade, two-dimensional (2D) materials such as graphene, transition metal dichalcogenides or Xenes have become an intensively studied topic, due to their unique properties that make them suitable for a wide range of applications such as nanoelectronics, spintronics, photonics or structural materials [1,2]. In recent years, 2D III-V materials, in particular 2D GaN, have been theoretically studied [3] and experimentally demonstrated [4].

In this work, we used first-principles calculations to uncover new structures of bilayer GaN. These structures are buckled and are shown to be more stable than the flat configuration. We then compared the electronic properties of buckled bilayer GaN with the flat bilayer. Finally, we studied the impact of compressive strain on their structure and properties.

2. Methodology

The structural and electronic properties of bilayer GaN are studied using the density functional theory (DFT). More specifically, we use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [5], with corrections for the van der Waals interactions as introduced by Grimme [6] and implemented in the Quantum Espresso software package [7]. The behavior of the core electrons is approximated using Projector Augmented-Wave (PAW) pseudopotentials. A vacuum region of at least 15 Å is set in the direction perpendicular to the layers to ensure that they do not interact with their periodic images.

First, new structures of bilayer GaN have been constructed, based on the 2×2×1, 3×3×1 and 4×4×1 super cells of bilayer GaN with an AA' stacking. Each structure is characterized by a series of digits $[x_1x_2...x_n]$ made of zeros and ones. The following convention was used to characterize each structure by a codeword $Opt\text{-}[x_1x_2...x_n]$ where the digits represented by $[x_1x_2...x_n]$ are set as follows:

1. The length of the codeword, n corresponds to the period of the repeated pattern.
2. A zero ($x_k = 0$) is given if the atom is located in-plane as it would be in the flat structures.
3. A one ($x_k = 1$) is given if the atom is out-of-plane (corresponding to buckling).

As examples, the flat structure is labelled by Opt-0 and the structure built from the 4×4×1, with an alternation of two in-plane atoms and two out-of-plane ones is labelled by Opt-1100. Schematic views of four models are presented in Fig. 1.

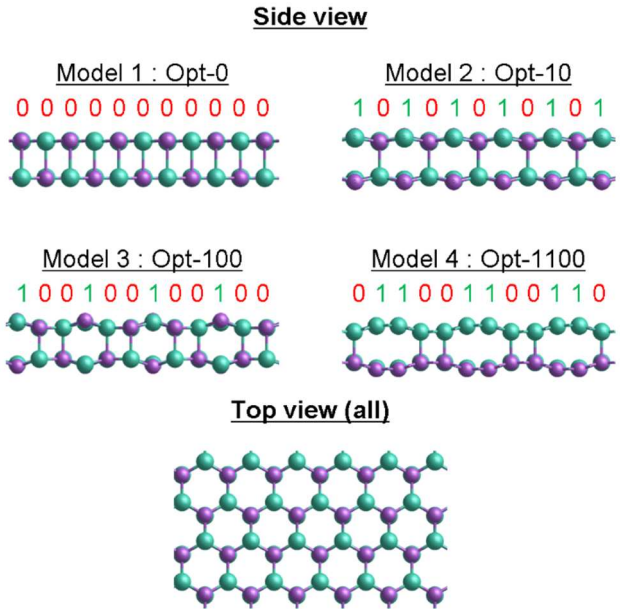

Fig. 1: Side and top views of four models of bilayer GaN. The codewords are also indicated. Ga (resp. N) atoms are colored in teal (resp. purple).

To study the atomic structures, the following three lengths are considered:

1. The average (short) interlayer distance d, between bonded atoms, denoted by ***d-distance***.
2. The average (buckled) interlayer distance b, between the sublayers of buckled atoms, denoted by ***b-distance***.
3. The average ***buckling parameter*** Δz, defined as Δz = (b-d)/2.

Table I: Summary of the properties computed for GaN structures

Configuration	Flat monolayer	Flat (Opt-0) bilayer	Opt-10 bilayer	Opt-100 bilayer	Opt-110 bilayer	Opt-1000 bilayer	Opt-1100 bilayer
Lattice a (Å)	3.22	3.27	3.24	3.25	3.24	3.26	3.24
Lattice b (Å)	3.22	3.27	3.25	3.25	3.24	3.26	3.24
Energy (eV/atom)	-2081.9900	-2082.1326	-2082.1374	-2082.1438	-2082.1410	-2082.1401	-2082.1434
Δ E (eV/atom)	0.154	0.011	0.006	0.000	0.003	0.004	0.000
Distance d (Å)	/	2.48	2.30	2.32	2.21	2.24	2.19
Distance b (Å)	/	/	2.90	3.12	2.93	3.00	3.09
Buckling parameter Δz (Å)	0.00	0.00	0.30	0.45	0.36	0.38	0.45
Band gap (eV)	2.09	1.93	1.81	1.95	1.89	1.91	1.91
Gap type	Indirect	Indirect	Indirect	Indirect	Indirect	Indirect	Direct

3. Results and discussion

The atomic structures of the different models are first relaxed. Then, the structural and electronic properties are evaluated. The results are summarized in Table I. The lattice parameters of the buckled structures are found to be lower than those of the flat bilayer. It turned out that the most stable models are the Opt-100 (Fig. 1, model 3) and Opt-1100 (Fig. 1, model 4) ones, with a total energy 0.011 eV/atom lower than the flat bilayer. The difference in energy between these two structures is below 0.001 eV/atom. All the structures built (with buckling) were found to have a lower energy than the flat bilayer. Therefore, the buckling mechanism allows the structure to relax to a more stable state. However, due to the small energy difference, different structures may coexist at room temperature. It is noteworthy that the d-distances range from 2.1 to 2.5 Å, while the b-distances are around 2.9-3.0 Å. Therefore, the protruding atoms are no longer bonded.

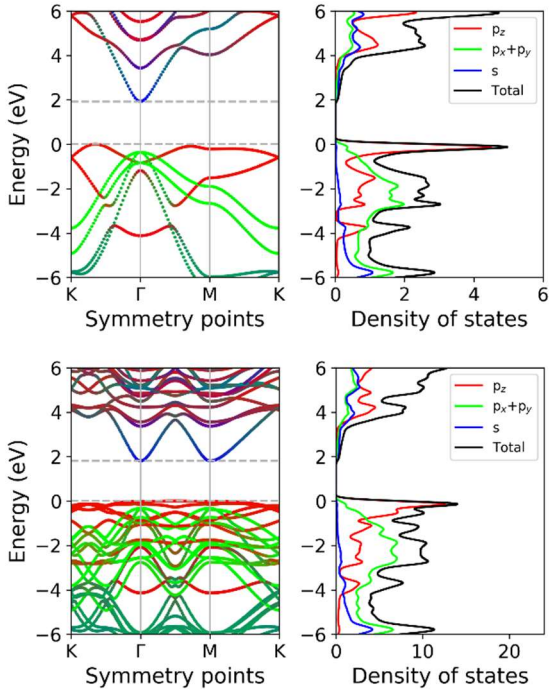

Fig. 2: Band structure and density of states of flat bilayer GaN (top) and of the Opt-10 structure (bottom). The colors reflect the contribution from different orbitals: Ga(s) in blue, N(p_z) in red and N(p_x+p_y) in green. The dashed lines indicate the position of the top of the valence band and of the bottom of the conduction band.

Interestingly, the electronic properties are impacted by the change in atomic structure from the flat configuration to buckled ones. Although the band gap is only slightly impacted (up to 0.15 eV of change), an indirect-to-direct gap transition is found in the Opt-1100 structure. A study of the band structure and of the density of states (DOS) reveal that the main change arises around the top of the valence band (TVB), due to the p_z orbitals of N, which are the most strongly impacted by buckling, as shown by the difference in height between the DOS peaks around the TVB, as illustrated by Fig. 2 for the flat bilayer (top) and for the Opt-10 (bottom) structures.

The impact of strain is studied by stretching the structure along both in-plane directions (bi-axial) or along one direction, either perpendicular to the buckling lines (uni-axial perpendicular) or parallel to them (uni-axial parallel). Our calculations reveal that a compressive strain favors the buckled structures, while a tensile one favors the flat ones. Also, under a compressive strain of 4 % or more, there is an indirect-to-direct band gap transition in all the configurations, with the TVB mainly dominated by the p_x and p_y orbitals of N.

4. Conclusions

New structures of bilayer GaN were uncovered and their properties were studied using first-principles calculations. We showed that the buckling of GaN layers leads to more stable configurations and it has a significant impact on the electronic properties, owing to the p_z orbitals of N. Under compressive strain, bilayer GaN show a transition from an indirect to direct band gap. Nevertheless, due to the small difference in energy between the different structures of bilayer GaN, they may coexist at room temperature.

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