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## On bilayer GaN: New stable structures and impact of hydrogen passivation

In the last decade, two-dimensional (2D) materials such as graphene, Xenes or hexagonal boron nitride (hBN) have been intensively studied, owing to their unique properties that make them potential building blocks for many applications in nanoelectronics, spintronics, photonics or structural materials. Recently, III-V 2D materials have been experimentally demonstrated, in particular 2D GaN [1]. While bulk GaN has a wurtzite atomic structure, monolayer GaN tends to adopt a hexagonal structure. For a bilayer, it remains unclear which type of atomic structure is preferred, since interactions at the interfaces may lead to surface relaxation or reconstruction, which in turn would have an impact on their electronic properties [2]. In this study, we used ab initio calculations to explore new structures of bilayer GaN, first in their pristine configurations, then with hydrogen passivation.

To study bilayer GaN, we performed density functional theory (DFT) calculations using the Quantum Espresso software package [3], with the Perdew-Burke-Ernzerhof exchange-correlation (PBE) functional, including corrections for the dispersion forces as introduced by Grimme [4]. In wurtzite GaN, three particular planes are generally considered, namely the a-plane  $[11\bar{2}0]$ , m-plane  $[1\bar{1}00]$  and c-plane  $[0001]$ , as illustrated in **Figure 1**. To build pristine bilayer structures, we considered a slice of bulk wurtzite GaN along the c-plane, which yield initial hexagonal structures, and study different types of buckling patterns (10,100,110,1100...) from super cells of bilayer GaN, as illustrated in **Figure 2**. Different stacking patterns are also studied (AA1, AA2...). For hydrogen-passivated bilayer GaN, in addition to the previous structures obtained by slices along the c-plane, we also considered structures obtained from slices along the a-plane and m-plane. Hydrogen passivation is performed by adding H atoms where dangling bonds are present to reform  $sp^3$ -type bonding. Different passivation patterns are considered (full, Ga-only, N-only, half) for the same stacking and buckling patterns as for the pristine case.

For pristine bilayer GaN, our results reveal that the most stable structure is neither the flat one nor the wurtzite-like one. In fact, several buckled structures have a lower energy, the lowest one being reached by the configuration with stacking pattern AA2 and buckling pattern 100, also labelled AA2-100, followed by the AA2-1100 one, with a small difference in energy, which hints at the coexistence of regions of different buckling pattern types at room temperature [5,6]. The occurrence of buckling stabilizes the atomic structure as  $sp^3$  bonding tend to be formed, and results in changes in the electronic structure [6], due to the (out-of-plane)  $p_z$  orbitals of N atoms. In the AA2-1100 configuration, this even leads to an indirect-to-direct band gap transition, as can be seen in **Figure 3**. Applying an external strain allows one to control the structure and electronic properties of bilayer GaN, as a tensile strain favors the flat bilayer structure with an indirect band gap, while a compressive strain favors buckled structures with a direct band gap.

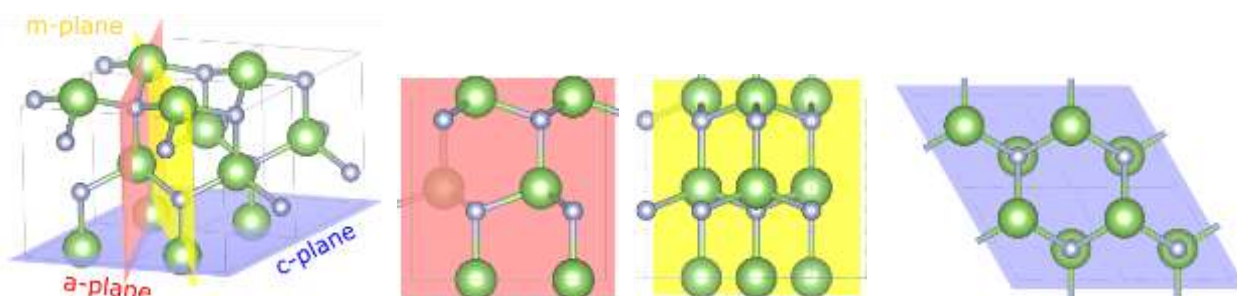
Passivation by H atoms to reform  $sp^3$  bonds potentially stabilizes the structure of bilayer GaN. Considering different stacking, buckling and passivation patterns, we studied the structure of bilayer GaN with a H concentration, that ranges from 12.5 % to 100 %, denoted by [H]. The H-concentration is defined by the ratio between the number of H atoms and the combined number of Ga and N atoms. It appears that for low [H] values (25% or less), the most stables structures are the ones obtained by a slice along the c-plane. However, for large [H] values, structures obtained by slices along the a- or m-plane are the most stable.

Using first principles calculations, we uncovered new structures of pristine bilayer GaN with a lower energy than both the flat and the wurtzite-like configurations. The occurrence of buckling leads to significant changes in the electronic properties. For instance, an indirect-to-direct band gap transitions occurs for some particular buckling patterns or under an applied strain. While for pristine bilayer GaN, the structures obtained by a slice along the c-plane are the most stable, for H-passivated structuration, the orientation of the most stable structure depends on the H concentration. These findings are promising for tuning the properties of GaN in future applications.

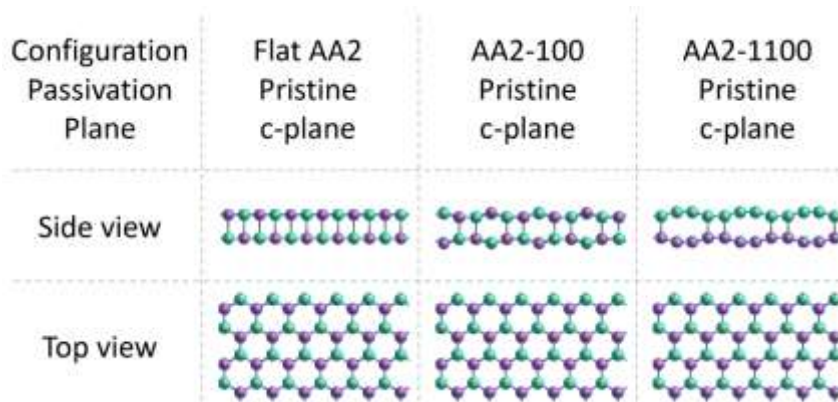
## References

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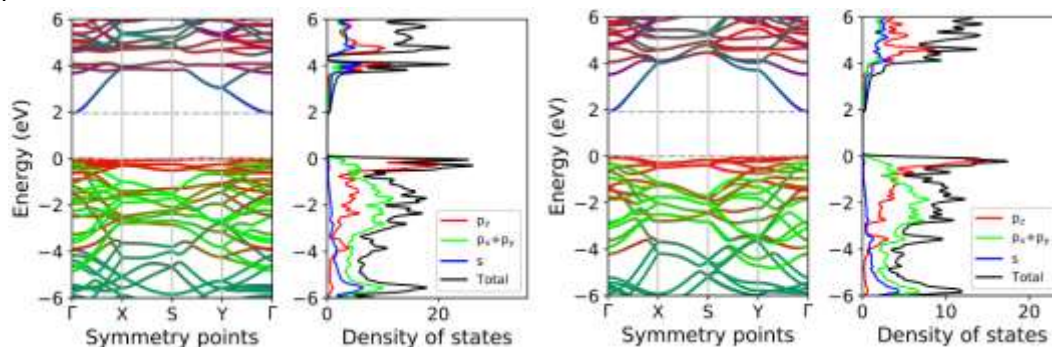
## Figures



**Figure 1:** Planes in bulk GaN (wurtzite). Ga (N) atoms are represented by large green (small blue) balls. The a-plane, m-plane and c-plane are colored in red, yellow and blue, respectively. The views normal to the a-plane, m-plane and c-plane are also shown.



**Figure 2:** Schematic view of several models of bilayer GaN. Ga, N atoms are colored in blue, purple, respectively. The type of stacking pattern, buckling pattern, passivation type is indicated as well as the plane along which the slice was performed.



**Figure 3:** Band structures and projected density of states of the pristine AA2-100 structure (left) and of the pristine AA2-1100 structure (right).