

## Electronic Structures and Magnetic Properties of GaN Sheets and Nanoribbons

Haiming Li,<sup>‡</sup> Jun Dai,<sup>§</sup> Jiong Li,<sup>‡,||</sup> Shuo Zhang,<sup>‡,||</sup> Jing Zhou,<sup>‡</sup> Linjuan Zhang,<sup>‡</sup>  
Wangsheng Chu,<sup>‡</sup> Dongliang Chen,<sup>‡</sup> Haifeng Zhao,<sup>‡</sup> Jinlong Yang,<sup>\*,†,§</sup> and Ziyu Wu<sup>\*,‡,⊥,#</sup>

*Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, People's Republic of China, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Pudong District, Shanghai 201204, People's Republic of China, National Synchrotron Radiation Lab, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, and Theoretical Physics Center for Science Facilities, Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

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First principles calculations were performed to study the electronic structures of gallium nitride (GaN) sheets and nanoribbons (NRs) in order to understand the influence of defects or edge states on magnetic properties. It is shown that the Ga-defective GaN sheet may be a good candidate for spintronics due to its half-metal property under certain conditions, even if a perfect GaN sheet is a nonmagnetic semiconductor. We investigated both zigzag and armchair GaN NRs with and without edge atoms passivated by H. The H-passivated GaN NRs and bare armchair NRs can be classified as nonmagnetic semiconductors. Band gap gradually decreases with the increase of the width of NRs. A ferromagnetic character occurs in bare zigzag GaN NRs with width of about 1.7 nm (mainly determined by edge Ga and N). Furthermore, we have shown that thin layer GaN NRs could also be ferromagnetic. Magnetic moment does not decrease to zero even up to six layers. Results offer a deeper understanding of the influence of both defects and edge states of GaN sheets and monolayer and multilayer NRs, particularly in terms of their structural and magnetic properties.

### I. Introduction

Nowadays, magnetic semiconductor materials are considered very interesting topics in the materials science community due to their high potential applications in spintronics.<sup>1,2</sup> Bulk semiconductors doped with different transition metals have been considered as the most promising room temperature-diluted magnetic semiconductor (DMS) compounds,<sup>3,4</sup> although underlying interaction mechanics remain unclear. Apart from the advantages of bulk magnetic semiconductor materials, nanoscale materials offer unique physical properties due to quantum confinement and surface effects. They also have high potential applications in new electronic, optical, electrochemical, and electromechanical devices. Interest in magnetism of nanoscale materials has recently increased significantly while new systems are being investigated. Several metal oxide nanoparticles like TiO<sub>2</sub>, ZnO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and CeO<sub>2</sub> without magnetic impurities have been studied by Sundaresan et al. and showed room temperature ferromagnetism.<sup>5</sup> Botello-Mendez et al. introduced a theoretical model describing the ferromagnetism and metallicity in ZnO zigzag nanoribbons (NRs) and claimed that ferromagnetism can be associated with oxygen-dangling bonds at the edge sites.<sup>6</sup> Other works on MoS<sub>2</sub><sup>7</sup> and SiC<sup>8</sup> zigzag NRs

also reveal ferromagnetism in nanomaterials. These discoveries on free transition metal nanoscale semiconductor materials with ferromagnetism have led to new developments in the exploration of magnetic semiconductors.

Due to its wide (3.4 eV) and direct band gap, gallium nitride (GaN) is a suitable material for applications in light-emitting devices that operate in the blue and ultraviolet region.<sup>9</sup> In the last two decades, GaN materials, from bulk to nanoscale, have been attracting increasing attention due to their performance in optics, electronics, and photoelectronics.<sup>10</sup> Huang et al. synthesized single crystal n-type GaN nanowires with electron mobility comparable or larger than the bulk and substantially larger than nanoscale FETs produced with carbon nanotubes.<sup>11</sup> Other types of GaN nanomaterials, such as nanotubes,<sup>12</sup> nanobelts,<sup>13</sup> and NRs,<sup>14,15</sup> were also synthesized. Although extensive experimental and theoretical effort has been devoted to the understanding of the properties of GaN nanostructure,<sup>16,17</sup> to our knowledge, almost no literature is available on the magnetism of GaN nanostructures. Moreover, it has been well-known that the electronic structure of nanostructure materials is strongly affected by the state of edge atoms or defects. For example, the edge of zigzag graphene NRs modified by NO<sub>2</sub> and CH<sub>3</sub> groups may be half-metallic, as discussed by Kan et al.<sup>18</sup> Xu et al. also showed that band gap changes between bare and passivated ZnO nanowires with hydrogen through first principles calculations.<sup>19</sup>

In this contribution, we present a study using density functional theory (DFT)<sup>20</sup> to investigate the electronic structure of 2-D GaN sheets and 1-D GaN NRs. We also investigate the role of defects and the edge effect in these systems.

\* Authors to whom correspondence should be addressed. E-mail: wuzy@ustc.edu.cn. (Z.W.) and jlyang@ustc.edu.cn (J.Y.).

<sup>‡</sup> Institute of High Energy Physics, Chinese Academy of Sciences.

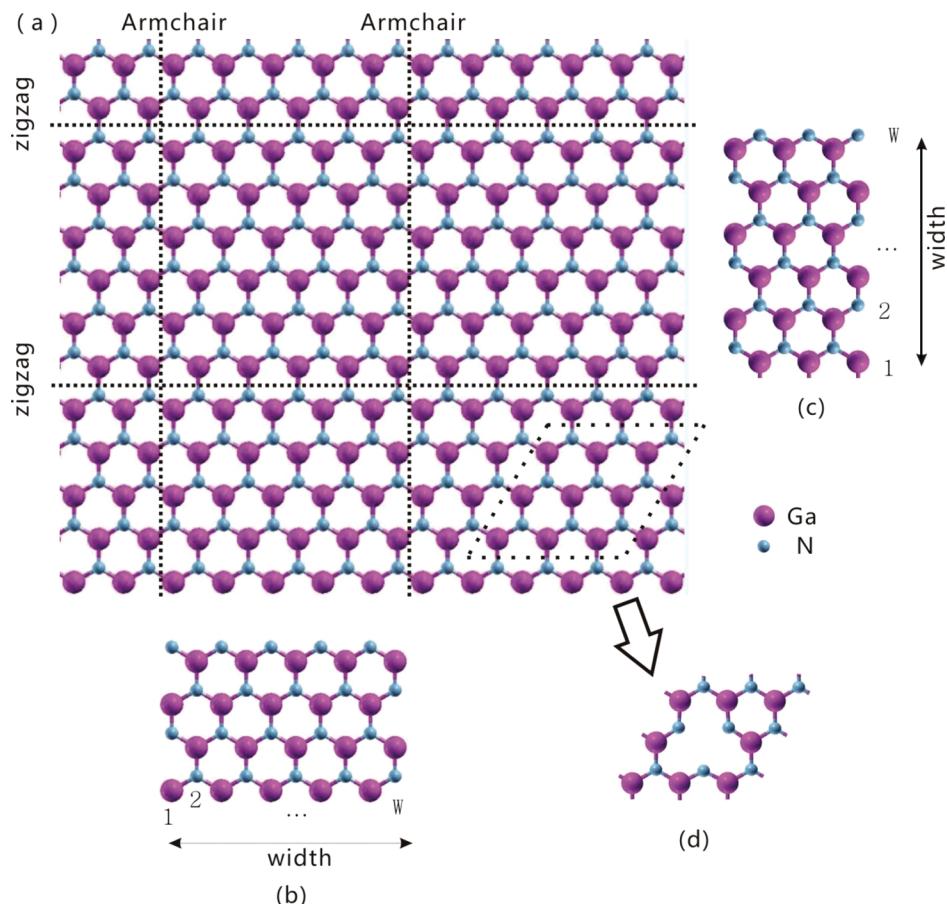
<sup>§</sup> Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China.

<sup>||</sup> Shanghai Institute of Applied Physics, Chinese Academy of Sciences.

<sup>†</sup> E-mail: jlyang@ustc.edu.cn.

<sup>⊥</sup> National Synchrotron Radiation Lab, University of Science and Technology of China.

<sup>#</sup> Theoretical Physics Center for Science Facilities, Chinese Academy of Sciences.



**Figure 1.** (a) The geometry of the 2D GaN sheet. Geometric structures of (b) armchair and (c) zigzag GaN NRs of width  $W$ , cut from both armchair and zigzag lines. (d) The supercell structure of the GaN sheet with a Ga-defect. The balls represent Ga atoms (purple) and N atoms (blue).

## II. Models and Computational Details

The DFT method has been widely employed to predict material properties. Herein, we present calculations performed using local density approximations (LDA) by the Vienna ab initio simulation package (VASP).<sup>21,22</sup> Electronic wave functions were expanded by using a plane-wave basis set with a cutoff energy of 500 eV. For armchair (zigzag) GaN NRs, the Brillouin zone integration for geometry optimizations was performed using a  $1 \times 1 \times 7$  ( $1 \times 1 \times 13$ ) Monkhost-Pack  $k$ -points grid.<sup>23</sup> The denser  $1 \times 1 \times 11$  ( $1 \times 1 \times 17$ )  $k$ -points were then incorporated into the self-consistent total energy and statics calculations. A  $6 \times 6 \times 1$  Monkhost-Pack  $k$ -points grid was used for the GaN sheet. All calculations were spin-polarized and the atomic positions of the structure were relaxed until all the force components were smaller than 0.025 eV/Å. The relaxed crystal structure and charge density were drawn with the XCrySDen package.<sup>24</sup>

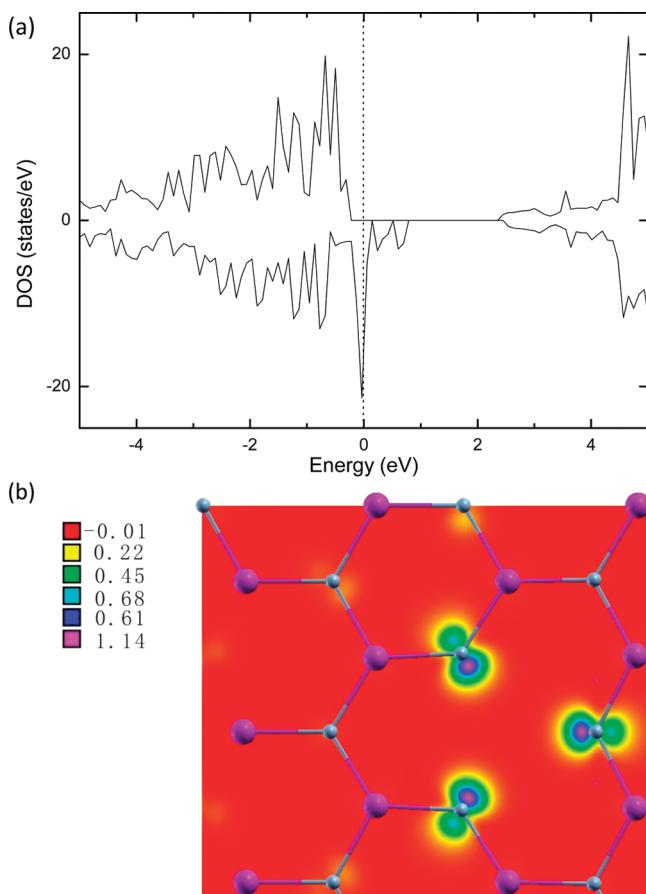
The GaN NRs studied herein were constructed by cutting a planar monolayer GaN (0001) sheet along two parallel lines, as shown in Figure 1. The NRs width,  $W$ , is defined as the number of dimer lines along the ribbon direction for the armchair GaN NRs, and the number of zigzag chains for the zigzag GaN NRs. To investigate the edge state effect, two geometries were considered, namely, bare GaN NRs and GaN NRs with dangling bonds at the ribbon edges saturated by hydrogen atoms.

## III. Results and Discussion

**a. 2D GaN Sheets.** The lattice constant of the calculated bulk GaN is  $a = 3.16$  Å,  $c = 5.14$  Å with an internal coordinate of

$u = 0.377$ . The average Ga–N bond length is 1.93 Å with a band gap of 2.0 eV, which is consistent with previous LDA calculations,<sup>25</sup> although slightly smaller than the experimentally determined lattice constant and band gap.<sup>26</sup> The discrepancy in values between those from experiment and calculations has to take into account the fact that the LDA calculations do not describe the electronic exchange correlation interactions accurately; the LDA always underestimates both lattice constant and band gap. Spin-polarized calculations show that both the bulk GaN and the 2-D GaN (0001) sheet are classified as nonmagnetic semiconductors. This is consistent with available data. However, dangling bonds induced by defects or the edge effect may be inherent in the new properties exhibited by nanoscale GaN materials.

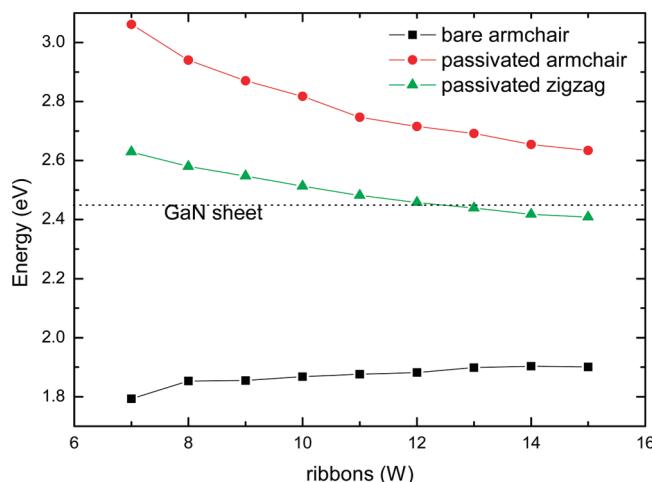
Although a perfect GaN sheet is nonmagnetic, Ga defects may induce intrinsic ferromagnetism. The GaN sheet supercell model was built, as shown in Figure 1d, with 8 Ga atoms and 9 N atoms in order to simulate Ga-defect concentration in the system. A global magnetic moment of  $3 \mu_B/\text{defect}$  was observed. Antiferromagnetic (AFM) ordering calculation was also performed. The energy is 80 meV/supercell higher than the energy of ferromagnetic (FM) ordering, implying that defects may interact in a ferromagnetic way. The density of state (DOS) of the GaN sheet with Ga defects is shown in Figure 2a. Fermi energy crossed the minority spin band, while it acted as a semiconductor for the majority spin band. The spin-polarized ratio is 100% at the Fermi energy while its conductivity is dominated by metallic single-spin states. This half-metallic system is a good candidate for spintronics. Spin density



**Figure 2.** (a) The total DOS. (b) The spatial spin distribution (up-down) of the GaN sheet supercell with a Ga-defect. Positive and negative sides are for spin-up and spin-down components, respectively. The balls represent Ga atoms (purple) and N atoms (blue).

distribution was plotted, as seen in Figure 2b. The three N atoms around a defect were evidently spin-polarized. Ga atoms at the second nearest neighbor of the defect contributed slightly to the ferromagnetic behavior (only  $0.02 \mu_B/\text{Ga}$ ). However, we found that the magnetic moment was not just localized at the defect; even for the third nearest neighbor of N atoms, the  $4.8 \text{ \AA}$  distance contributed more than  $0.1 \mu_B/\text{N}$ . We then considered a more diluted (15 Ga atoms and 16 N atoms corresponding to 3.1% Ga-defect concentration) and higher concentration (3 Ga atoms and 4 N atoms corresponding to 12.5% Ga-defect concentration) model. Results indicate the same magnetic moment and similar half-metal characteristics from the FM ordering calculations. However, AFM ordering was more stable at a total energy of 17 and 40 meV lower than FM ordering, respectively. Moreover, previous calculations have shown that the Ga-defects may induce an intrinsic localized magnetism in the bulk GaN, suggesting semiconductor properties.<sup>27</sup> It is very interesting that we have obtained a half-metallic character in this 2-D case under particular defect concentrations.

**b. GaN NRs.** For the bare GaN NRs, we found that the edge N atoms tend to relax closer to the ribbons at a Ga–N bond length of  $1.76 \text{ \AA}$ . However, the edge Ga atoms relax significantly less than N atoms such that the Ga–N bond length changed to about  $1.83 \text{ \AA}$ . Atoms in the inner part relax less as well, and the Ga–N bond length was retained at  $\sim 1.82 \text{ \AA}$  similar to the GaN sheet. For H-passivated GaN NRs, the modified lengths of Ga–H and N–H bonds were  $1.54$  and  $1.02 \text{ \AA}$ , respectively. The Ga–N bonds found close to the edge changed at a lesser rate than in bare geometry due to the charge balance



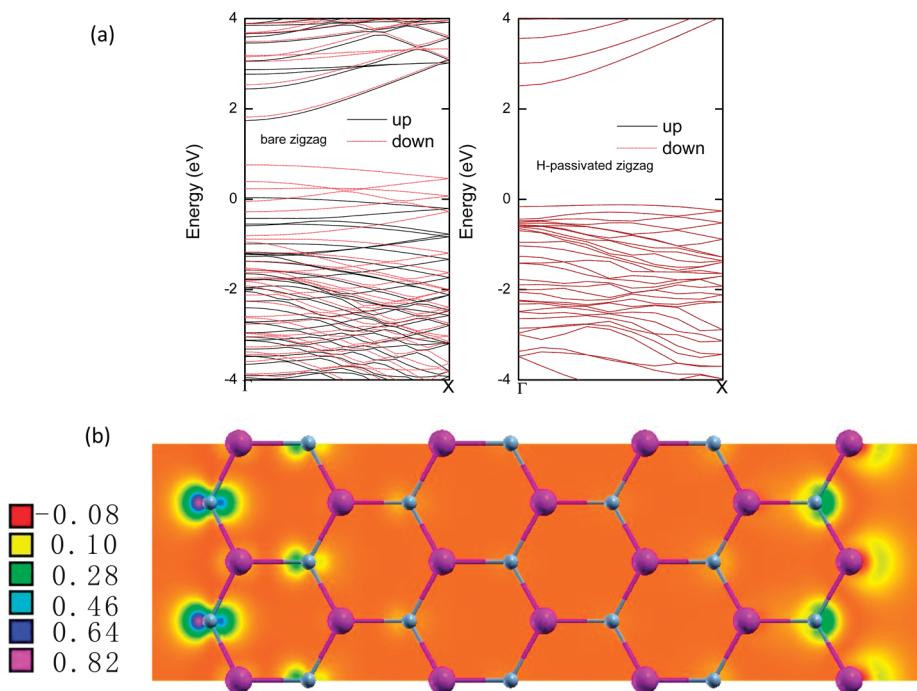
**Figure 3.** The band gap behavior of bare armchair, H-passivated armchair, and bare zigzag GaN NRs as a function of the width.

at the edge. The edge N bond with an inner Ga obtained a bond length of  $1.80 \text{ \AA}$ , while the edge Ga bond with the inner N obtained a bond length of  $1.83 \text{ \AA}$ .

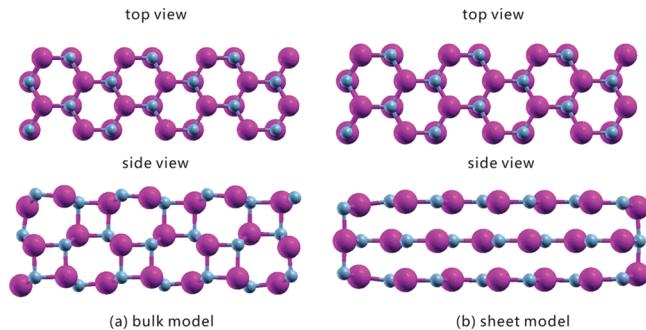
The other systems, excluding the bare zigzag GaN NRs that are ferromagnetic, are classified as nonmagnetic and semiconductors. Their band gap behavior versus width ( $W$ ) is shown in Figure 3. For the H-passivated geometry, the band gap of both armchair and zigzag GaN NRs decreased with  $W$ . We know that, in normal cases, as the size of the nanomaterials increases, the band gap decreases, apart from them tending to concentrate close to the bulk. However, it would be interesting to note that as  $W$  increased, the band gap of H-passivated zigzag GaN NRs routed through the band gap of the GaN sheet, and the band gap of the bare armchair GaN NRs increased. It has been well established that band gap increases with  $W$ ; the trend of the band gap in an infinite set of GaN sheets is determined by the weakening of the quantum size effect. The disagreement is probably due to edge states, which also affected the nanoscale system. Nakamura et al.<sup>28</sup> observed a similar behavior in H-passivated zigzag BN NRs. As pointed out in their work, at small dimensions, edge states play an important role for both the highest occupied valence band (HOVB) and the lowest unoccupied conduction band (LUCB), which is sensitive to the band gap value.

The band structures of bare and zigzag GaN NRs are plotted in Figure 4a. The figure also shows the magnetic character of bare GaN zigzag NRs, whose resulting magnetic moment is  $1.72 \mu_B$  for  $W = 7$ , which is twice as large as that for ZnO NRs.<sup>6</sup> The spin density distribution in Figure 4b shows that the unpaired spin mainly concentrates at Ga and N atoms at the edge, while inner Ga and N atoms contribute with a small amount of unpaired spins. Closer to the center the magnetic moment of the inner atom is smaller. When the NRs width is small, such as when  $W = 7$ , the magnetic moment of inner atoms allows a weak ferromagnetic coupling. Increasing the NRs width it is expected that the interaction from magnetic moments at both edges becomes weaker, and the total magnetic moment is mainly determined by the edge effect. We calculated the size effect on the magnetic properties. Increasing the width, the magnetic moment decreases from  $1.72 \mu_B$  for  $W = 7$  to  $1.45 \mu_B$  for  $W = 15$ . We also considered a larger NR with  $W = 19$ , i.e., with about 5 nm width, obtaining a magnetic moment of  $1.43 \mu_B$ .

**c. Multilayer GaN NRs.** Due to the unusual magnetic properties exhibited by the single-layer bare zigzag GaN NRs,

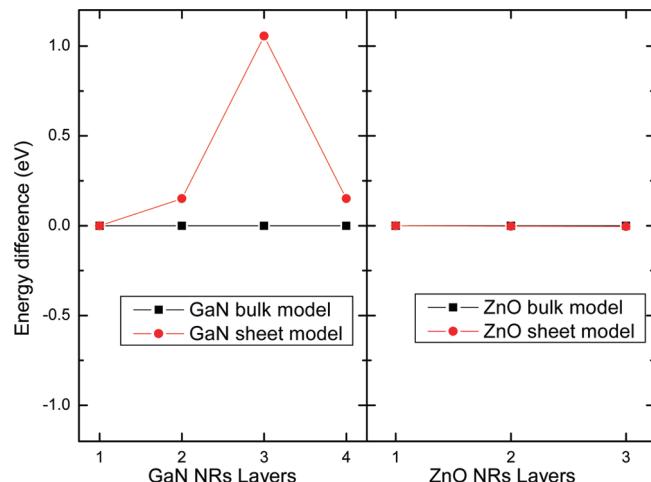


**Figure 4.** (a) The band structure of bare and H-passivated zigzag GaN NRs with  $W = 7$ . (b) The spin density distribution of a bare zigzag GaN NRs with  $W = 7$ .



**Figure 5.** Relaxed structures of three layers of GaN NRs based on the bulk model (left) and the sheet model (right). Colors are the same as in Figure 1.

We further investigated the stacked effect of this kind of GaN NRs. Multilayer GaN NRs were cleaved from the bulk GaN directly with several Ga–N layers (bulk model). The width of the ribbons was set to  $W = 7$  in our calculations. The relaxed structure of three-layer GaN NRs is shown in Figure 5a. The hexatomic ring character was observed when the GaN sheet was shown from the top view. The inner atoms, from the side view, bonded close to 2.0 Å, and a shape similar to bulk GaN was achieved. In terms of the spin density distribution of the single-layer bare GaN NRs, the Ga and N atoms at the edge were both found to contribute to ferromagnetism. For multilayer GaN NRs, the edge of the 2p level of N atoms and the sp level of the Ga atom mainly contributed to the magnetic moment. The resulting magnetic moments are  $1.6 \mu_B/\text{layer}$ , zero,  $0.66 \mu_B/\text{layer}$ , and  $0.5 \mu_B/\text{layer}$  for ribbons from one to four GaN NRs layers, respectively. The works of Botello-Mendez et al. have shown that multilayer ZnO NRs are nonmagnetic at an even-numbered layer, while the magnetic moment for odd-numbered layer GaN NRs quickly vanishes as the layer number increases to five layers. We have calculated six layers of GaN NRs with a magnetic moment of about  $0.8 \mu_B/\text{layer}$ . Therefore, the GaN NRs may be a better choice for spin electronic use, even for the case of the multilayer. Our results clearly demonstrate that



**Figure 6.** Comparison of the total energy between GaN (left) and ZnO (right) NRs, using the bulk and the sheet model with different layers.

the very thin layer of GaN NRs could possess ferromagnetism even at the pure state of the GaN semiconductor system, suggesting the absence of any transition metal impurities.

We further showed that our bulk model is a better model, unlike the sheet model (stack GaN NRs layer-by-layer with particular distance), in simulating the relaxation of multilayer GaN NRs. The sheet model was used to simulate the relaxation of GaN NRs. The relaxed three-layer GaN NRs is shown in Figure 5b. Only the edge atoms between layers were bonded, and the inner part of each layer showed a rough smoothing. The energy difference of the relaxed structure was compared between the bulk model and the sheet model. On the basis of total energy, as shown in Figure 6, the bulk model was found to be more stable than the sheet model. Thus, the bulk model is more appropriate for the calculations, as compared to the sheet model, which always converged with the metastable structure. The same comparison is employed for ZnO NRs. Total energy

calculations show that both models have very close results (less than 2 meV) (Figure 6). These results reveal that the calculated model is system-dependent on the multilayer NRs system, and its selection is very important in achieving reasonable results.

#### IV. Conclusions

In conclusion, we presented an investigation of both the electronic and magnetic properties of a GaN sheet and GaN NRs with armchair- or zigzag-shaped edges. We have shown that edge states in GaN NRs affect both electronic structure and magnetic properties. Moreover, both armchair and H-passivated zigzag GaN NRs, independent of width, always show a wide band gap; the edge states affect the band structure in nanoscale. Bare zigzag GaN NRs presented magnetic properties, and Ga and N atoms at the edges were observed as the main contributor to the magnetic moment. We showed that very thin layers of GaN NRs could possess ferromagnetism even up to six layers. The two models for the multilayer were compared by NRs calculations. It was demonstrated that only the bulk model could converge to ground state structures, and that the choice of model is system-dependent. We also observed from calculations that, in this 2-D system, Ga-defects may induce a half-metallic configuration, an interesting discovery for dedicated spintronics device application. Results have provided a deeper understanding of the influence of defect and edge state on GaN sheet and NRs, especially in magnetism. We believe that our theoretical results will motivate further experimental work related to the synthesis and characterization of a very thin ferromagnetic GaN sheet and NRs.

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