Applied Physics Letters

RESEARCH ARTICLE | JANUARY 31 2011

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Appl. Phys. Lett. 98, 053102 (2011)
https://doi.org/10.1063/1.3549299

AIP Publishing

APPLIED PHYSICS LETTERS **98**, 053102 (2011)

Tailoring band gap in GaN sheet by chemical modification and electric field: *Ab initio* calculations

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(Received 5 October 2010; accepted 7 January 2011; published online 31 January 2011)

Ab initio calculations show that the GaN monolayer (GaN-ML) in (0001) face is a planar semiconductor with an indirect band gap of 1.95 eV. The gap converts into a direct one and is enlarged by 0.81 eV when the GaN-ML is modified by H and F atoms. Furthermore, the gap can be efficiently manipulated in a range of 1.8 to 3.5 eV by applying an external electric field. Moreover, because of the spontaneous polarization, the gap is remarkably broadened by a positive electric field while it is rapidly decreased under a negative field. The chemical modification also significantly improves the stability of GaN-ML. © *2011 American Institute of Physics*. [doi:10.1063/1.3549299]

Gallium nitride (GaN) has attracted great attention over the past decade due to its intriguing optoelectronic properties and high thermal and mechanical stability. With the large band gap (~3.4 eV) and the advent of epitaxial growth techniques, GaN is widely used in efficient short-wavelength (blue and ultraviolet) light-emitting diodes (LEDs) and room-temperature laser diodes.[1,2] Through band-gap engineering, GaN based materials are promising to overcome the "green valley of death"[3] and go infrared, thus achieving the applications on full color display.[4] Currently, band-gap engineering is mainly manipulated via In or Al alloying, which, however, has the handicaps of a low composition rate and local fluctuations in the In or Al fraction.[5] Therefore, other ways to engineer the band gap of GaN based materials are always desirable if possible.

In recent years, semiconductor nanostructures have come under extensive investigation for both scientific research and technological applications.[6–8] GaN based nanowires, nanotubes, and nanospirals have been synthesized and showed great potential for fabricating wide-spectrum LEDs and other nanoscale devices.[9–11] In particular, a recent theoretical study predicted that a GaN sheet transforms into a two dimensional (2D) graphitic structure when it is in the form of an ultrathin film.[12] The atomic thin hexagonal 2D nanostructures such as graphene[13] and boron nitride nanosheets[14] have attracted considerable interest due to their unique electronic properties, which, in many cases, should be more fruitful than corresponding bulk structures. Moreover, on-plane chemical modification and an external electric field have been reported to greatly tailor the band structures of such 2D based materials.[15–17] Consequently, the possible unique optical and luminescent properties of 2D GaN nanosheets stimulate our study of whether a tunable band gap could be obtained via chemical modification or external electric field. In this letter, we carry out first-principles calculations on the electronic structure of a GaN monolayer (GaN-ML) with or without chemical modification and under an external electric field. Our calculations show that the band gap of GaN-ML increases when the sheet is modified with H and F atoms. Of particular interest is the feasibility of large ranged tunable band gaps in such a 2D structure under the external electric field, which may open opportunities for these GaN based materials in optoelectronic devices.

Our calculations were performed within a general gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE)[18] of density functional theory (DFT), as implemented in VASP code.[19] Projected augmented wave method[20] is employed to describe the electron-ion potential and a kinetic energy cutoff of 500 eV is selected for the plane wave expansion. We used a $2\times2\times1$ super cell and a $9\times9\times1$ k-point grid for the Brillouin zone. The vacuum space between two layers is about 12 Å, which was found large enough to avoid any artificial interaction. The effect of the electric field is implemented by adding an artificial dipole sheet in the vacuum part.[21]

The pristine GaN-ML is cut from its wurtzite crystal terminated with the $(0001/000\bar{1})$ polar surface. The optimized structure is a planar nonpolar 2D hexagonal atomic thick film with D_{3h} symmetry, as shown in Fig. 1. The calculated Ga–N bond length is 1.87 Å, inconsistent with previous LDA calculations,[22,23] and is smaller than its wurtzite bulk value of 1.94 Å.[24] The cohesive energy is -8.06 eV per Ga–N pair, which is calculated by subtracting the total energy of Ga and N free atoms from that of optimized GaN-ML. This energy is about 0.8 eV higher than that of a GaN wurtzite structure (-8.85 eV). The cohesive energy of ZnO-ML is -8.42 eV, which is also about 0.5 eV higher than that of a ZnO wurtzite structure.[25] With the rapid development in synthesis and the existence of single layers as BN

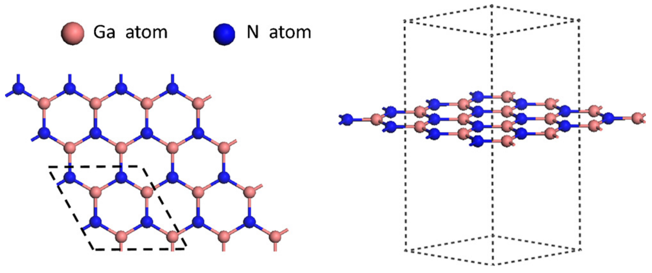

FIG. 1. (Color online) Top and side views of the optimized GaN-ML. The rhombus plotted in dashed line represents the super cell adopted in the calculations.

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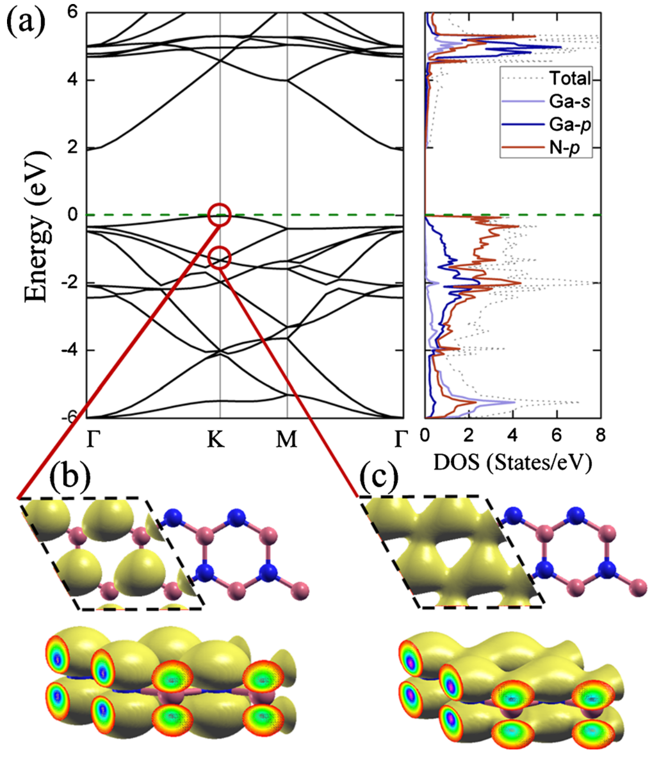

FIG. 2. (Color online) (a) Band structure and PDOS of the pristine GaN-ML and corresponding charge densities, (b) and (c), of the VBM at the K points labeled with two circles, respectively. The isovalue is 0.005 e/Å^3.

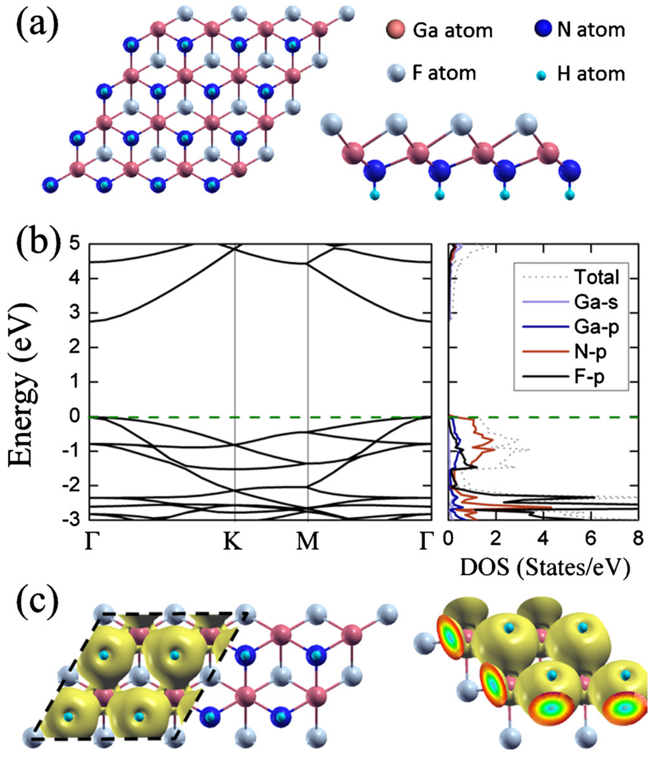

FIG. 3. (Color online) (a) Top and side views of the optimized FGaNH-ML. (b) Band structure and PDOS of the FGaNH-ML and corresponding charge densities (c) of the VBM at the Γ point. The isovalue is 0.005 e/Å^3.

and ZnO,[26] the fabrication of GaN-ML should be feasible experimentally in the near future. The electronic band structures and partial densities of states (PDOS) for the GaN-ML are plotted in Fig. 2(a). From this, we can observe an indirect band gap of 1.95 eV and the bands near the valence band maximum (VBM) is dominated by the N-*p* orbitals. To have a detail understanding of the band structure, we further plot the partial charge density of these bands at the K point labeled with circles in Figs. 2(b) and 2(c). One can see that the Ga and N atoms in such a planar structure show significant sp^2+p_z hybridization. Most of the N-p_z electrons are quite localized, forming nonbonding orbitals and few of them hybrid with the nearby Ga atoms forming π bonds. This is inconsistent with the covalent-ionic bonding characteristic of Ga–N bonds resulting from their different electronegativities and is different from graphene, in which the carbon atoms have equal status; thus, all of the C-p_z electrons can form π bonds with each other.[13]

The nonbonding N-p_z orbitals at VBM [Fig. 2(b)] might make the pristine GaN-ML more chemically active and less stable than graphene. Therefore, we used hydrogen to saturate the N atoms.[27] The hydrogen prefers the top site of N atoms with N–H bonds arranged normal to GaN-ML, similar to the semihydrogenated graphene sheet.[28] Meanwhile, saturation of N atoms breaks the π-bonding network and the 4*s* and 4*p* electrons of Ga atoms become localized and unpaired. Thus, those bands composed of Ga-*s*,*p* orbitals are pushed to the VBM and even across the Fermi level. This suggests that the semidydrogenated GaN-ML might not be chemically stable and the Ga atoms should also be saturated.

Considering the different electronegativities of H and F, we used fluorine atoms to saturate the Ga atoms on the other side of the semihydrogenated GaN-ML. The relaxed GaN-ML modified with H and F atoms on both sides (FGaNH-ML) [Fig. 3(a)] is wrinkled and the F atoms prefer to stay on the hollow sites of the hexagonal GaN-ML and bond with the three nearest Ga atoms, which is analogous with the fluorinated ZnO layers.[29] Band structure and related PDOS [Fig. 3(b)] show that the FGaNH-ML is a semiconductor with a direct band gap of 2.76 eV, significantly larger than the indirect gap of GaN-ML. This is due to the presence of the bonding orbitals between N and H atoms [see Fig. 3(c)], which brings down the energy of the VBM dominated by the nonbonding N-*p* orbitals and thus enhances the chemical stability of GaN-ML. As regular DFT calculation generally underestimates the band gaps, we made GW calculations (which the self-energy is the product of the single-particle Green function G and the screened interaction W) for both GaN-ML and FGaNH-ML to quantitatively compare with future experimental data. The GW band gaps are calculated to be 4.14 and 5.87 eV for GaN-ML and FGaNH-ML, respectively, which are both about 2.5 eV larger than those obtained from DFT. Thus, although DFT could not calculate the band gap correctly, it is powerful to predict a correct trend and to properly demonstrate the physical mechanism.[30,31] Considering the extremely expensive computational cost of the GW method, especially in the presence of an external electric field, we stick to the DFT/PBE method for all the related calculations as we mainly focus on the changes of the band gaps.

To further engineer the band gap and improve the luminescence properties of such a 2D GaN based material, we study the electronic structure of FGaNH-ML under an external field. The electric field is added perpendicularly to the nanosheet with different electric strengths ranging from −6 to 6 V/nm. Here, we defined the positive direction of the

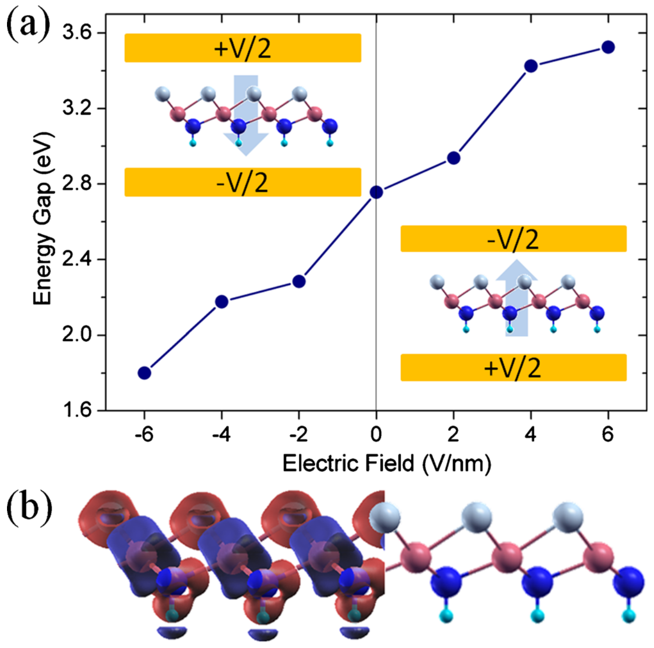

FIG. 4. (Color online) (a) Band gap of FGaNH-ML vs electronic fields. (b) The CDD of FGaN-ML. The isovalue is 0.03 e/Å^3. The geometry structure is also placed on the right for contrast.

external electric field as pointing from the H side to the F side. As shown in Fig. 4(a), the band gap exhibits a nearly linear dependence on the electric field strength and varies from 1.8 to 3.5 eV. More interestingly, the gap is significantly broadened by a positive electric field while it is rapidly decreased under a negative field. This may be understood as follows: Due to the different electronegativity, the electrons transfer from H side to the F side, as can be seen from the charge density difference (CDD) plotted in Fig. 4(b). Thus, the opposite ionic charges at the two sides induce a spontaneous polarization across the FGaNH-ML in the same direction as the positive field, which results in the different response of the band gap when the external electric field turns around.

To study the stability of the FGaNH-ML, we calculated the formation energy E_f per unit cell defined as

$$E_{f1} = E_{FGaNH} - E_{GaN} - 1/2E_{H2} - 1/2E_{F2} \qquad (1)$$

$$E_{f2} = E_{FGaNH} - E_{GaN} - E_{HF} \qquad (2)$$

Where E_{FGaNH} and E_{GaN} are the energies of FGaNH-ML and GaN-ML and E_{H2}, E_{F2}, and E_{HF} are the energies of isolate H_2, F_2, and HF molecules, respectively. The formation energies E_{f1} and E_{f2} are -4.22 and -1.50 eV per unit cell, respectively. Both of the negative values indicate that the FGaNH-ML is energetically stable. In addition, the E_{f1} of FGaNF-ML, HGaNH-ML, and HGaNF-ML are -3.58, -0.80, and -0.47 eV, respectively, which are all higher than that of FGaNH-ML, showing the highly stability of FGaNH-ML.

In summary, we have studied the stability and the electronic properties of the pristine GaN-ML via density functional theory with and without H or/and F atoms modification. We found that the presence of H and F atoms can significantly enhance the thermal stability of the GaN-ML and turn it from an indirect semiconductor to a direct one accompanying an enlarged band gap. Moreover, we further revealed that the external electric field can efficiently tune the band gap of FGaNH-ML ranged from 1.8 to 3.5 eV. More interestingly, because of the spontaneous polarization in FGaNH-ML, the band gap is remarkably broadened by a positive electric field while it is rapidly decreased under a negative field. This large gap variation, which is sensitive to the electric field direction and strength, might bring possibilities for the next generation optoelectronic devices, such as optoelectronic sensor or full color LEDs.

This work is supported by the NBRP (Grant Nos. 2010CB923401, 2011CB302004, and 2009CB623200), NSF (Grant Nos. 11074035 and 20873019), SRFDP (Grant No. 20090092110025), the Outstanding Young Faculty Grant, and the Peiyu Foundation of SEU in China. The authors thank the computational resource at Department of Physics, SEU.

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