Energy Gaps and Stark Effect in Boron Nitride Nanoribbons

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A first-principles investigation of the electronic properties of boron nitride nanoribbons (BNNRs) having either armchair or zigzag shaped edges passivated by hydrogen with widths up to 10 nm is presented. Band gaps of armchair BNNRs exhibit family-dependent oscillations as the width increases and, for ribbons wider than 3 nm, converge to a constant value that is 0.02 eV smaller than the bulk band gap of a boron nitride sheet owing to the existence of very weak edge states. The band gap of zigzag BNNRs monotonically decreases and converges to a gap that is 0.7 eV smaller than the bulk gap due to the presence of strong edge states. When a transverse electric field is applied, the band gaps of armchair BNNRs decrease monotonically with the field strength. For the zigzag BNNRs, however, the band gaps and the carrier effective masses either increase or decrease depending on the direction and the strength of the field.

Two-dimensional crystals, including graphene and single layer of hexagonal boron nitride (BN), have recently been fabricated [1]. Among them, only graphene has been studied extensively [2]. Unlike graphene, a hexagonal BN sheet is a wide gap insulator like bulk hexagonal BN [3] and is a promising material in optics and optoelectronics [4].

Graphene nanoribbons (GNRs) [5] with width a few to a hundred nanometers have been produced by lithographical patterning [6, 7] or chemical processing [8] of graphene. We expect that boron nitride nanoribbons (BNNRs) could also be made using similar or other techniques. Figures (a) and (b) show the structures of an armchair BNNR with N_a dimer lines (N_a-aBNNR) and a zigzag BNNR with N_z zigzag chains (N_z-zBNNR), respectively. A tight-binding study of the bandstructures of 21-aBNNR and 13-zBNNR (corresponding to widths ~ 3 nm) [9] and first-principles investigations of the electronic properties of small width BNNRs [10, 11] have been reported. However, to our knowledge, first-principles calculations on the electronic properties of experimentally realizable size of BNNRs have not been performed.

Under a transverse electric field, carbon nanotubes with impurity atoms are expected to show novel band gap opening behaviors [12], whereas zigzag GNRs reveal half-metallicity [13]. On the other hand, single-walled boron nitride nanotubes (SW-BNNTs), which are rolled up BN sheets [14, 15, 16], have been predicted to show gigantic Stark effect in their band gaps in response to a transverse electric field [17], and this effect has been confirmed experimentally [18]. The effect becomes stronger in larger diameter SW-BNNTs [17]. A similar phenomenon is expected in BNNRs. Unlike SW-BNNTs, however, BNNRs can be arbitrarily wide. Therefore, the consequences of the Stark effect in BNNRs would be even more dramatic than in SW-BNNTs.

In this study, we report first-principles calculations on the electronic properties of armchair and zigzag BNNRs up to width of 10 nm with hydrogen passivation of the edge carbon atoms. We show that the band gaps of armchair and zigzag BNNRs do not converge to the same value even when the ribbons are very wide. The band gap of armchair BNNRs, obtained by density functional theory (DFT) calculations within the local density approximation (LDA), converges to a value that is 0.02 eV smaller than the LDA band gap of 4.53 eV of a BN sheet [19]. Unlike armchair GNRs, the lowest unoccupied band of the armchair BNNRs is composed of edge states with energy position asymptote to a fixed value when the ribbon is wider than 3 nm, the decay length of the edge-state. The band gap of the zigzag BNNRs, also determined by edge states, is monotonically reduced as a function of increasing width and converges to a value that is 0.7 eV smaller than the LDA bulk gap because, as discussed below, of an additional edge polarization charge effect. The DFT Kohn-Sham eigenvalues within LDA in general underestimate the band gaps of materials; an accurate first-principles calculation of band gaps requires a
The quasiparticle approach was used. The basic physics discovered here however should not be changed.

When a transverse electric field is applied, the highest occupied and the lowest empty states in armchair BNNRs become localized at the two different edges. Because of the external electrostatic potential difference between the two edges, the band gap is reduced with increased field strength. On the contrary, in zigzag BNNRs, depending on the field direction, the states near the band gap either become more localized at the edges or less so. Also, the band gaps and effective masses either decrease or increase depending on field strength and direction. These novel properties could be used in manipulating the transport properties of doped BNNRs.

We performed ab initio pseudopotential DFT calculations within LDA in a supercell configuration using the SIESTA computer code. A double-zeta plus polarization basis set was used and ghost orbitals were included to describe free-electron-like states. A charge density cutoff of 300 Ry was used and atomic positions were relaxed so that the force on each atom is less than 0.04 eV/Å. To eliminate spurious interactions between periodic images, a supercell size of up to 20 nm × 20 nm in the xz plane was used.

The armchair BNNRs are found to have a direct gap at the zone center [left panel of Fig. 2(a)]. The highest occupied state, the valence band maximum (VBM), has a wavefunction which is localized at nitrogen atoms throughout the ribbon [right lower panel of Fig. 2(a)]. The lowest empty state, the conduction band minimum (CBM), is however an edge state with wavefunction localized at the boron atoms on the edges [right upper panel of Fig. 2(a)]. In contrast, the corresponding state for an armchair GNRs is delocalized throughout the ribbon.

The total potential near the edge of the armchair BNNRs is different from that of the bulk. By incorporating this variation into the on-site potential energies of a few BN dimer lines near the edges, one could reproduce the main features of the states near the band gap within a tight-binding formulation.

The zigzag BNNRs have the VBM at a point between the X and the Γ points which has wavefunction localized at the nitrogen edge and the CBM at the X point which has wavefunction localized at the boron edge. In the corresponding state for an armchair GNRs is delocalized throughout the ribbon. The total potential near the edge of the armchair BNNRs is different from that of the bulk. By incorporating this variation into the on-site potential energies of a few BN dimer lines near the edges, one could reproduce the main features of the states near the band gap within a tight-binding formulation.

Figure 4(a) shows the squared electron wavefunctions of the CBM states of 14-aBNNR and 26-aBNNR integrated in the yz plane. These states are localized on the boron atoms near the two edges. When the width is about 3 nm as in the 26-aBNNR, the wavefunction from the two edges begins to decouple and thus stablizes its energy position.

In zigzag BNNRs, the boron edge and the nitrogen edge are negatively and positively charged (electronic plus ionic charge), respectively. Because of this polarization, the potential felt by electrons is higher at the boron edge and lower at the nitrogen edge, contribut-
FIG. 3: (color online) LDA energy bandstructure (left) and the squared wavefunctions integrated along $z$ of the highest occupied state (right lower) and the lowest unoccupied state (right upper) of $7$-$z$BNNR under an external electric field $\vec{E}_{\text{ext}}$ of strength (a) zero, (b) $0.1$ eV/Å and (c) $-0.1$ eV/Å along the $x$ direction. Dashed red lines in the bandstructure indicate the energies of the band edge states. In the wavefunction plots, green regions are associated with high densities.

Figure 2(b) shows how the bandstructure and wavefunctions of a $14$-$a$BNNR change under a $0.1$ eV/Å transverse electric field. Owing to the Stark effect, the wavefunctions of the highest occupied and the lowest unoccupied states now localize at the opposite edges where the external electrostatic potential felt by an electron is higher and lower, respectively [right panel of Fig. 2(b)]. Thus, the band gaps of armchair BNNRs decrease when a transverse electric field is applied [left panel of Fig. 2(b)].

FIG. 4: (color online) (a) Band gaps of armchair (filled red squares) and zigzag (empty blue squares) BNNRs versus their widths. Inset: band gaps of armchair BNNRs versus $N_a$ (see Fig. 1). Solid lines are a guide to the eyes. Dashed lines indicate the bulk band gap of a BN sheet with no edges. (b) Probability distributions $|\Phi(r)|^2$ integrated in the $yz$ plane (see Fig. 1) versus the distance along the $x$ direction from the ribbon center for the lowest unoccupied state in $14$-$a$BNNR (solid red line) and $26$-$a$BNNR (dashed blue line). (c) The effective polarized line charge density $\sigma_{\text{eff}}$ of zigzag BNNRs versus $w_z$. The solid line is a guide to the eyes.

defined as

$$\sigma_{\text{eff}} \equiv \hat{x} \cdot \frac{1}{w_z h_z} \int_{\text{unit cell}} dr \rho(r) r$$

where $\rho(r)$ is the total charge density including the core charge, and $h_z$ the spatial period along the $y$ direction [see Fig. 1(b)], decreases as $\sim 1/w_z$ [Fig. 4(c)] due to an increased screening, resulting in the decrease and convergence of the band gap as $w_z$ increases.

Figure 2(b) shows how the bandstructure and wavefunctions of a $14$-$a$BNNR change under a $0.1$ eV/Å transverse electric field. Owing to the Stark effect, the wavefunctions of the highest occupied and the lowest unoccupied states now localize at the opposite edges where the external electrostatic potential felt by an electron is higher and lower, respectively [right panel of Fig. 2(b)]. Thus, the band gaps of armchair BNNRs decrease when a transverse electric field is applied [left panel of Fig. 2(b)].

Regarding a factor which increases the band gap of the narrow $z$BNNRs since the VBM and the CBM are edge-states localized at the nitrogen edge and the boron edge, respectively [Fig. 3(a)]. However, as the ribbon becomes wider, the effective polarization line charge density $\sigma_{\text{eff}}$,
Effective hole masses (in units of the free electron mass $m_0$) of the highest occupied band in 36-aBNNR (filled red circles) and 84-aBNNR (empty blue squares) under a transverse electric field versus the field strength. The inset in (a) shows energy gaps as a function of the external potential difference between the two edges. (b) and (d): Similar quantities as in (a) and (c) for 27-zBNNR (filled red circles) and 46-zBNNR (empty blue squares), respectively.

Figure 5: (color online) (a) and (c): LDA energy gaps and effective hole masses (in units of the free electron mass $m_0$) of the highest occupied band in 36-aBNNR (filled red circles) and 84-aBNNR (empty blue squares) under a transverse electric field versus the field strength. The inset in (a) shows energy gaps as a function of the external potential difference between the two edges. (b) and (d): Similar quantities as in (a) and (c) for 27-zBNNR (filled red circles) and 46-zBNNR (empty blue squares), respectively.

A similar behavior has been predicted \cite{17} and observed \cite{18} in BNNTs.

Figures 3(b) and 3(c) show how the bandstructure and the edge-state wavefunctions of a 7-zBNNR change under a 0.1 eV/Å transverse electric field. When an electric field is applied toward $+x$ direction, the VBM and CBM edge-state wavefunctions do not change qualitatively [right panel of Fig. 3(b)]. Thus, for a similar reason as in the armchair BNNRs, the band gap decreases [left panel of Fig. 3(b)]. When the electric field is applied along $-x$ direction, the potential felt by an electron localized at the right edge (the nitrogen edge) is decreased whereas that at the left edge (the boron edge) is increased. Therefore, the energy gap between these two states increases as shown in Fig. 3(c). (Actually, the energy of the original lowest empty state has been increased. Therefore, the energy gap between these two states increases as shown in Fig. 3(c)).

Figures 5(a) and 5(b) show the band gap variation of BNNRs with field strength. In armchair BNNRs, the band gap decreases when the field strength increases regardless of its direction [Fig. 5(a)]. A similar behavior has been observed in SW-BNNTs \cite{17}. For example, for the 10 nm wide 84-aBNNR the LDA band gap is reduced from 4.5 eV to less than 1.0 eV under a 0.1 eV/Å field. In zigzag BNNRs, at small field strength, the band gap decreases when the field is along $+x$ direction but increases when the field is reversed [Fig. 5(b)]. In other words, zigzag BNNRs show asymmetric Stark effect. However, as the field becomes stronger, the band gap decreases regardless of the direction. Moreover, the band gap variations, when plotted against the difference in the external electrostatic potential between the two edges, fall on a universal curve for ribbons with different widths [insets of Figs. 5(a) and 5(b)]. This is because the gap determining states localize on different edges as the field becomes strong; thus, the change in their energy difference is directly related to the potential difference between the edges.

Figures 5(c) and 5(d) show the effective mass of the hole carrier at the VBM for a range of external field strength. In armchair BNNRs, the hole mass of the VBM is independent of the field strength. In contrast, the corresponding effective mass in zigzag BNNRs changes with the external field, and even more interestingly, in an asymmetric way. In particular, when the field is along $-x$ direction, the effective mass decreases substantially. Within $\pm0.02$ eV/Å variation of the field, the effective mass can be varied by 50% from 0.6 $m_0$ to 0.9 $m_0$ where $m_0$ is the free electron mass. In the case of electron carriers in zigzag BNNRs, a nearly-free-electron state \cite{9,17,22} becomes the CBM if a field stronger than a critical value, depending on the width, is applied [see Fig. 5(c)], and the characteristics of charge carriers change significantly. These novel phenomena demonstrate the possibility of tuning carrier mobilities of doped BNNRs by applying a transverse electric field.

In summary, we have studied the electronic properties of BNNRs as a function of width with or without an external transverse electric fields. The band gap of the armchair BNNR and that of the zigzag BNNR are determined by edge-states and thus converge to values different from that of the bulk BN sheet. The electronic and the transport properties of BNNRs are shown to be tunable by an external transverse electric field. Especially, zigzag BNNRs are shown to exhibit asymmetric response to the electric field.

Additional remark: After completion of the work and during the preparation of this manuscript, we became aware of a related work on similar systems from other group \cite{20}.

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