Electrically Tunable Quasi-Flat Bands, Conductance and Field Effect Transistor in Phosphorene

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Phosphorene, a honeycomb structure of black phosphorus, was isolated recently. We investigate electric properties of phosphorene nanoribbons based on the tight-binding model. A prominent feature is the presence of quasi-flat edge bands entirely detached from the bulk band. We explore the mechanism of the emergence of the quasi-flat bands analytically and numerically from the flat bands well known in graphene by a continuous deformation of a honeycomb lattice. The quasi-flat bands can be controlled by applying in-plane electric field perpendicular to the ribbon direction. The conductance is switched off above a critical electric field, which acts as a field-effect transistor. The critical electric field is anti-proportional to the width of a nanoribbon. This results will pave a way toward nanoelectronics based on phosphorene.

Graphene is one of the most fascinating material found in this decade. The low-energy theory is described by massless Dirac fermions, which leads to various remarkable electrical properties. In practical applications to current semiconductor technology, however, we need a finite band gap in which electrons cannot exist freely. For instance, armchair graphene nanoribbons have a finite gap depending on the width, while bilayer graphene under perpendicular electric field also has a gap. It is desirable to find an atomic monolayer bulk sample which has a finite gap. Silicene is one of the promising candidates of post graphene materials, which is predicted to be a quantum spin-Hall insulator. A striking property of silicene is that a topological phase transition is induced by applying electric field. Nevertheless, silicene has so far been synthesized only on metallic surfaces. Another promising candidate is a transition metal dichalcogenides such as molybdenites.

A new comer challenges the race of the post-graphene materials. That is phosphorene, a honeycomb structure of phosphorus. It has been successfully obtained in the laboratory and revealed a great potential in applications to electronics. Black phosphorus is a layered material where individual atomic layers are stacked together by Van der Waals interactions. Just as graphene can be isolated by peeling graphite, phosphorene can be similarly isolated from black phosphorus by the mechanical exfoliation method. As a key structure it is not planer but puckered due to the height of the puckered structure. Although we can control the band structure experimentally, we need a finite band gap, which is large enough. We propose a field-effect transistor driven by the ratio \( t_2/t_1 \). The flat bands are detached from the bulk band when the ratio is 2, while the flat bands are bent by the term \( t_4 \).

It is an exciting problem to control the band structure externally. We may change the band gap by applying external electric field \( E_z \) perpendicular to the phosphorene sheet with the use of the puckered structure. Although we can control the band gap, the amount of the controlled gap is very tiny compared to the large band gap, that is, \( \Delta = 1.52\text{eV} \) since the height of the puckered structure \( \ell \) is the order of nm. On the other hand, the quasi-flat edge band is found to be sensible to external electric field \( E_x \) parallel to the phosphorene sheet. This is because a large potential difference (\( \propto W E_x \)) is possible between the two edges if the width \( W \) of the nanoribbon is large enough. We propose a field-effect transistor driven by in-plane electric field with the use of the quasi-flat edge bands. The conductance is shown to be either 0 or \( 2e^2/h \) with respect to the in-plane electric field. If the nanoribbon width is \( 1\mu m \), the critical electric field is given by \( E_{cr} = 0.15\text{meV/nm} \). This is experimentally feasible.

4-band tight-binding model. The unit cell of phosphorene contains 4 phosphorus atoms, where two phosphorus ex-
been shown that it is enough to take hopping links, as illustrated in Fig.2. The Brillouin zone of the 2-band model is constructed by folding the hexagonal Brillouin zone of the 2-band model: The two bands are precisely common between the two models, while the extra two bands in the 4-band model are obtained simply by shifting the two bands of the 2-band model, as dictated by the folding of the Brillouin zone.

In the representation the 4-band Hamiltonian reads as \( \hat{H}_4 = \sum_k c^\dagger(k) \hat{H}_4(k)c(k) \) with

\[
\hat{H}_4 = \begin{pmatrix}
0 & f_1 + f_3 & f_4 & f_2 + f_5 \\
 f_1^* + f_3^* & 0 & f_2 & f_4 \\
f_2 & f_4 & 0 & f_1 + f_3 \\
f_2^* & f_4^* & f_1^* & f_3^* & 0
\end{pmatrix},
\]

where

\[
f_1 = 2t_1 e^{ik_x/2} \cos \frac{\sqrt{3}}{2} k_y, \quad f_2 = t_2 e^{-ik_x},
\]

\[
f_3 = 2t_3 e^{-5ik_x/2} \cos \frac{\sqrt{3}}{2} k_y,
\]

\[
f_4 = 4t_4 \cos \frac{3}{2} k_x \cos \frac{\sqrt{3}}{2} k_y, \quad f_5 = t_5 e^{2ik_x}.
\]

We show the Brillouin zone and the energy spectrum of the tight-binding model in Fig.3(a) and (c), respectively.

**2-band tight-binding model.** We are able to reduce the 4-band model to the 2-band model due to the \( C_{2h} \) point group invariance. We focus on a blue point (atom in upper layer) and view other lattice points in the crystal structure (Fig.1). We also focus on a red point (atom in lower layer) and view other lattice points. As far as the transfer energy is concerned, the two views are identical. Namely, we may ignore the color of each point. Hence, instead of the unit cell containing 4 points, it is enough to consider the unit cell containing only 2 points. This reduction makes our analytical study considerably simple.

The 2-band model is given by \( \hat{H}_2 = \sum_k c^\dagger(k) \hat{H}_2(k)c(k) \) with

\[
\hat{H}_2 = \begin{pmatrix}
f_4 \\
f_4 + f_5 + f_3 + f_5^* \\
f_4 + f_3 + f_5 + f_5^* \\
f_4 + f_5 + f_3 + f_5^*
\end{pmatrix}.
\]

The rectangular Brillouin zone of the 4-band model is constructed from that of the 2-band model, as illustrated in Fig.2(a).

The equivalence between the two models (2) and (4) is verified as follows. We have explicitly shown the energy spectra of the 4-band model (2) and the 2-band model (4) in Fig.2(c) and (d), respectively. It is demonstrated that the energy spectrum of the 4-band model is constructed from that of the 2-band model: The two bands are precisely common between the two models, while the extra two bands in the 4-band model are obtained simply by shifting the two bands of the 2-band model, as dictated by the folding of the Brillouin zone.

**Phosphorene nanoribbons.** We investigate the band structure of a phosphorene nanoribbon placed along the \( y \) direction (Fig.1). We study zigzag and beard edges. There are three types of nanoribbons, whose edges are (a) both zigzag, (b) zigzag and beard, (c) both beard. We show their band structures in Fig.3(a), (b) and (c), respectively.

A prominent feature is the presence of the edge modes isolated from the bulk modes found in Fig.3(a) and (b). They comprise a quasi-flat band. It is doubly degenerate for a zigzag-zigzag nanoribbon, and nondegenerate for a zigzag-beard nanoribbon, while it is absent in a beard-beard nanoribbon [Fig.3(c)].

**FIG. 2:** Brillouin zones and energy spectra of the 4-band and 2-band models of phosphorene. (a) The Brillouin zone is a rectangular in the 4-band model, which is constructed from two copies of the hexagonal Brillouin zone of the 2-band model. A magenta oval denotes a Dirac cone present at the \( \Gamma \) point. (b) The Brillouin zone is a hexagonal in the 2-band model. A magenta oval denotes a Dirac cone present at the \( M \) point. (c) The band structure of the 4-band model, which is constructed from two copies of that of the 2-band model. (d) The band structure of the 2-band model.

**FIG. 3:** Band structure of phosphorene nanoribbons when the transfer energy \( t_4 \) is nonzero and zero. (a,d) Both edges are zigzag. (b,e) One edge is zigzag and the other edge is beard. (c,f) Both edges are beard. The quasi-flat edge mode emerges for (a) and (b). When we set \( t_4 = 0 \), the quasi-flat band becomes perfectly flat band. Flat and quasi-flat Edge states are marked in magenta.
Let us explore the mechanism how such an isolated quasi-flat band appears in phosphorene. By diagonalizing the Hamiltonian, the energy spectrum reads

\[ E(k) = f_4 \pm |f_1 + f_2 + f_3 + f_5| \tag{5} \]

The band gap is given by

\[ \Delta = 4t_1 + 2t_2 + 4t_3 + 2t_5 = 1.52 \text{ eV}. \tag{6} \]

The asymmetry between the positive and negative energies arises from the \( f_1 \) term. Then it is interesting to see what would happen when we set \( t_4 = 0 \). We show the band structures in Fig.\( 3d,e,f \) for the three types of nanoribbons, where the quasi-flat edge modes are found to become perfectly flat. Consequently it is enough to show the emergence of the flat band by studying the model with \( t_4 = 0 \). Furthermore it is a good approximation to set \( t_3 = t_5 = 0 \), since the transfer energies \( t_1 \) and \( t_2 \) are much larger than the others. Indeed we have checked numerically that no qualitative difference is induced by this approximation.

**Flat bands in anisotropic honeycomb lattice.** To explore the origin of the isolated quasi-flat band we analyze the anisotropic honeycomb-lattice model, which is described by the Hamiltonian \( H \) by setting \( f_3 = f_1 = f_5 = 0 \). This Hamiltonian is well studied in the context of graphene and optical lattice. The energy spectrum reads

\[ E = \sqrt{t_2^2 + 4 \left( t_1^2 + t_1 t_2 \cos \frac{3}{2} k_x \right) \cos \frac{\sqrt{3}}{2} k_y}, \tag{7} \]

which implies the existence of two Dirac cones at

\[ k_x = \pm \arctan(\sqrt{4t_2^2 - t_2^2/t_1^2}), \quad k_y = 0, \tag{8} \]

for \( |t_2| < 2 |t_1| \).

We now study the change of the band structure of nanoribbon by a continuous deformation of the honeycomb lattice, starting that of graphene. We show the band structure with (a) the zigzag-zigzag edges, (b) the zigzag-beard edges, and (c) the beard-beard edges in Fig.\( 4 \) for typical values of \( t_1 \) and \( t_2 \).

(i) We start with the isotropic case \( t_1 = t_2 \), where the energy spectrum \( E(k) \) becomes that of graphene with two Dirac cones at the \( K \) and \( K' \) points. The perfect flat band connects the \( K \) and \( K' \) points, that is, it lies for (a) \( -\pi \leq k \leq -\frac{\pi}{2} \) and \( \frac{3\pi}{2} \leq k \leq \pi \); (b) \( -\pi \leq k \leq \pi \); (c) \( -\frac{\pi}{2} \leq k \leq \frac{\pi}{2} \). It is attached to the bulk band. See Fig.\( 4a,b,c \). The topological origin of flat bands in graphene has been thoroughly discussed.

(ii) As we increase \( t_2 \) but keeping \( t_1 \) fixed, the two Dirac points move towards the \( \Gamma \) point (\( k = 0 \)), as is clear from Fig.\( 4 \). The flat band keeps to be present between the two Dirac points. See Fig.\( 4d,e,f \).

(iii) At \( |t_2| = 2 |t_1| \), the two Dirac points merge into one Dirac point at the \( \Gamma \) point, as implied by Fig.\( 4 \). The flat band touches the bulk band at the \( \Gamma \) point for the zigzag-zigzag nanoribbon and the zigzag-beard nanoribbon, but disappears from the beard-beard nanoribbon. See Fig.\( 4g,h,i \).

(iv) For \( |t_2| > 2 |t_1| \), the bulk band shifts away from the Fermi level, as follows from (7). The flat band is disconnected from the bulk band for the zigzag-zigzag nanoribbon and the zigzag-beard nanoribbon, where it extends over all region \( -\pi \leq k \leq \pi \). On the other hand, the edge band becomes a part of the bulk band and disappears from the Fermi level for the beard-beard nanoribbon. See Fig.\( 4j,k,l \).

**Energy spectrum of quasi-flat bands.** We have explained how the flat band appears in the anisotropic honeycomb-lattice model. The flat band is bent into the quasi-flat band by switching on the transfer interaction \( t_4 \).

We can derive the energy spectrum of the quasi-flat band perturbatively. We construct an analytic form of the wave function at the zero-energy state in the anisotropic honeycomb-lattice model \( (t_3 = t_4 = t_5 = 0) \). By solving the Hamiltonian matrix recursively from the outer most cite, we obtain the analytic form of the local density of states of the wave function for odd cite \( j \),

\[ |\psi(j)| = \alpha^3 \sqrt{1 - \alpha^2}, \tag{9} \]

with \( \alpha = 2|t_1|/(\cos \frac{\pi}{4}/|t_2|) \). The wave function is zero for even cite. It is perfectly localized at the outer most cite when \( k = \pi \), and describes the flat band. With the use of this wave function, the energy spectrum \( E_{qf}(k) \) of the quasi-flat band is estimated perturbatively by taking the expectation value of the \( t_4 \) term as

\[ E_{qf}(k) = -\frac{4t_1 t_4}{t_2} (1 + \cos k) \text{ eV}, \tag{10} \]

where \( 4t_1 t_4/t_2 = 0.14 \). On the other hand we numerically obtain \( E(0) = -0.301 \text{ eV} \). The agreement is excellent.
Phosphorene nanoribbons with in-plane electric field. It is an intriguing problem to control the band structure externally. We may try to change the band gap by applying external electric field $E_z$ perpendicular to the phosphorene sheet. We find the band gap to behave as

$$\Delta = 1.52 + 0.28(\ell E_z)^2 \text{eV},$$

where $\ell$ is the separation between the upper and lower layers. The gap becomes simply larger when we apply $E_z$. Furthermore, in practical applications, it needs very large electric field since $\ell$ is the order of nm.

On the other hand, it is possible to make a significant change of the quasi-flat edge band by applying external electric field parallel to the phosphorene sheet. Let us apply electric field $E_x$ into the $x$ direction of a nanoribbon with zigzag-zigzag edges. A large potential difference ($\propto W E_x$) is possible between the two edges if the width $W$ of the nanoribbon is large enough. This potential difference resolves the degeneracy of the two edge modes, shifting one edge mode upwardly and the other downwardly without changing their shapes. We present the resultant band structures in Fig.5 for typical values of $E_x$.

**Field-effect transistor.** Electric current may flow along the edge. We show the conductance in Fig.5. Without in-plane electric field, the conductance at the Fermi energy is $2e^2/h$ since there is a two-fold degenerate quasi-flat band. Above the critical electric field, the conductance becomes 0 since the quasi-flat band splits perfectly. This acts as a field-effect transistor driven by in-plane electric field. The critical electric field is anti-proportional to the width $W$.

We derive the critical electric field $E_{cr}$. The energy shift at $k = \pi$ is given by $\Delta E(\pi) = \pm WE_x$ since the wave function is perfectly localized at the outer most edge cite. In general the energy shift is given by

$$\Delta E(k) = \pm \left( W - \frac{\alpha^2}{1 - \alpha^2} \right) E_x.$$

It is well approximated by $\Delta E(k) = \pm WE_x$ for wide nanoribbons. The conductance is written as

$$\frac{e^2}{h} [\theta(E - \varepsilon_0 - |\Delta E(0)|) - \theta(E - |\Delta E(\pi)|)] + \theta(E - \varepsilon_0 + |\Delta E(0)| - \theta(E + |\Delta E(\pi)|)],$$

where $\theta(x)$ is the step function $\theta = 1$ for $x > 0$ and $\theta = 0$ for $x < 0$. The critical electric field is determined as

$$E_{cr} = |\varepsilon_0|/(2W).$$

If the nanoribbon width is $1\mu m$, the critical electric field is given by $E_{cr} = 0.15\text{meV}/\text{nm}$. This is experimentally feasible.

**Discussion.** We have analyzed the band structure of phosphorene nanoribbons based on the tight-binding model, and demonstrated the presence of quasi-flat edge modes entirely detached from the bulk band. Starting from the well-known structure of graphene, we have explained the mechanism how such edge modes emerge by a continuous deformation of the honeycomb lattice. The conductance due to the quasi-flat edge modes is quantized to be either 0 or $2e^2/h$ with respect to the in-plane electric field $E_x$. The critical electric field is $E_{cr} = 0.15\text{meV}/\text{nm}$ for a nanoribbon with width $1\mu m$. A field-effect transistor is possible with the use of this property. We may also expect a similar structure made of arsenic and antimony, which should be called as "arsenene" and "antimonene". The electronic properties will be explained simply by setting the transfer energies appropriately.

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Supporting Materials

Wave function of edge state. We construct an analytic form of the wave function at the zero-energy state in the anisotropic honeycomb-lattice model \((t_3 = t_4 = t_5 = 0)\) as follows. We label the wave function of the atom on the outermost cite as \(\psi_1\), and that of the atom next to it as \(\psi_2\), and as so on. The total wave function is \(\psi = \{\psi_1, \psi_2, \cdots, \psi_N\}\) if there are \(N\) atoms across the nanoribbon. The Hamiltonian is explicitly written as

\[
H = \begin{pmatrix}
0 & t_1g^* & 0 & 0 & \cdots \\
t_1g & 0 & t_2 & 0 & \cdots \\
0 & t_2 & 0 & t_1g^* & \cdots \\
0 & 0 & t_1g & 0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix},
\]

with \(g = 1 + e^{ik}\). The eigenvalue problem \(H\psi = 0\) is trivially solved, yielding \(\psi_{2n} = 0\) and \(\psi_{2n+1} = [t_1 (1 + e^{ik})] / t_2 \psi_1\).

The dispersion of the quasi-flat band is determined as

\[
E_{qf}(k) = \sum_{n=0}^{\infty} t_4 (1 - e^{-ik}) \psi_n^* \psi_{n+2} + t_4 (1 + e^{ik}) (\psi_{n+2}^* \psi_n) = -\frac{4t_1t_4}{t_2} (1 + \cos k),
\]

which is (10) in the text. The energy shift due to the in-plane electric field is given by

\[
\sum_{n=0}^{\infty} (W - n) |\psi_n|^2 = \left( W - \frac{\alpha^2}{1 - \alpha^2} \right) E_x,
\]

which is (12) in the text.

Electric field. We apply electric field \(E_z\) perpendicular to the sheet. It is necessary to use the 4-band tight-binding model, since the electric field breaks the \(C_{2h}\) point group invariance. Namely, the upper and lower layers are distinguished by the electric field. We introduce \(E_z\) into the Hamiltonian (2).

\[
\hat{H}_4(E_z) = \hat{H}_4 + \text{diag}(\ell E_z, \ell E_z, -\ell E_z, -\ell E_z).
\]

By diagonalizing this Hamiltonian at \(k = 0\), the band gap is found to be

\[
\Delta = \sum_{s=\pm 1} \sqrt{(t_2 + s4t_4 + t_5)^2 + (\ell E_z)^2} + 4 (t_1 + t_3),
\]

which yields numerically (11) in the text.

Low-energy theory. In the vicinity of the \(\Gamma\) point, we make a Taylor expansion and obtain

\[
f_1 = t_1 \left( 2 + ik_x - \frac{1}{4} k_x^2 - \frac{3}{4} k_y^2 \right),
\]

\[
f_2 = t_2 \left( 1 - ik_x - \frac{1}{2} k_x^2 \right),
\]

\[
f_3 = t_3 \left( 2 - 5ik_x - \frac{25}{4} k_x^2 - \frac{3}{4} k_y^2 \right),
\]

\[
f_4 = t_4 \left( 4 - \frac{9}{2} k_x^2 - \frac{3}{2} k_y^2 \right),
\]

\[
f_5 = t_5 \left( 1 + 2ik_x - 2k_y^2 \right).
\]

The Hamiltonian (4) reads

\[
\hat{H}_2 = f_4 + (\varepsilon + \alpha k_x^2 + \beta k_y^2) \tau_x + \gamma k_x \tau_y,
\]

with the Pauli matrices \(\tau\), where

\[
\varepsilon = 2t_1 + 2t_2 + t_3 + t_5 = 0.76 \text{eV},
\]

\[
\alpha = -\frac{1}{4} t_1 - \frac{1}{2} t_2 - \frac{25}{4} t_3 - \frac{9}{4} t_4 - 2t_5 = 0.336 \text{eV},
\]

\[
\beta = -\frac{3}{4} t_1 + \frac{3}{4} t_3 + \frac{3}{2} t_4 = 0.604 \text{eV},
\]

\[
\gamma = -t_1 + t_2 + 2t_3 - 2t_5 = 3.97 \text{eV}.
\]

Hence the dispersion is linear in the \(k_y\) direction but parabolic in the \(k_x\) direction. The low-energy Hamiltonian agrees with the previous result with a rotation of the Pauli matrices \(\tau_x \mapsto \tau_z\) and \(\tau_y \mapsto \tau_x\).

Conductance. In terms of single-particle Green’s functions, the low-bias conductance \(\sigma(E)\) at the Fermi energy \(E\) is given by

\[
\sigma(E) = (e^2 / h) \text{Tr} [\Gamma_L(E) G_D^{\dagger}(E) \Gamma_R(E) G_D(E)],
\]

where \(\Gamma_{\text{RL}(L)}(E) = i[\Sigma_{\text{RL}(L)}(E) - \Sigma_{\text{R}(L)}(E)]\) with the self-energies \(\Sigma_L(E)\) and \(\Sigma_R(E)\), and

\[
G_D(E) = [E - H_D - \Sigma_L(E) - \Sigma_R(E)]^{-1},
\]

with the Hamiltonian \(H_D\) for the device region. The self-energy \(\Sigma_{\text{RL}(L)}(E)\) describes the effect of the electrode on the electronic structure of the device, whose the real part results in a shift of the device levels whereas the imaginary part provides a life time. It is to be calculated numerically. We have used this formula to derive the conductance in Fig.
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