Disorder effect on mass-asymmetry in monolayer black phosphorus

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Abstract. In this work, we calculated the band structure for the monolayer black phosphorus (phosphorene) from the slater-Koster tight-binding method, where the effect of s-p mixing is considered. Using the new parameters, we studied the electronic properties of phosphorene. The electronic properties were calculated using the recursive Green’s Function method. From the resistance calculation, we showed that electrons in the ZZ directions had an effective mass ten times larger than those in the AC direction, which agrees with experimental results. We investigated the effect of disorder on the anisotropy of the effective mass and we showed that the intrinsic anisotropy is robust to the presence of disorder.

1. Introduction

The promising prospect of two-dimensional (2D) materials for technological applications has led to intensified research activities to uncover their physical properties. One of the most widely studied systems has been graphene, a one-atom-thick layer of carbon, with extraordinarily enhanced electronic properties that arise due to the quantum confinement of the carriers that act as relativistic massless Dirac fermions [1, 2]. Unfortunately, graphene does not have a natural bandgap that could be used for device application purposes. This reduces graphene’s potential as a replacement for the conventional semiconductor implemented in logical circuits.

In the last years, researchers have been searching for strategies to overcome graphene’s deficiencies; they are trying to convert graphene into a semiconductor by bonding oxygen to the graphene sheet[3] or by applying an external electric field on the bilayer. Both changes alter graphene’s electronic structure, turning it into a conventional semiconductor. However, these approaches have brought other problems; for example, graphene oxide’s electronic properties are strongly affected by molecules that interact with it, reducing the mobility and created puddles on the graphene sheets. Elemental layers of silicon, germanium, and very recently of black phosphorus (silicene, germanene, and phosphorene, respectively) have been considered as strong candidates for nanotechnology-based on 2D materials[4]. Today, many electronic, mechanical, optical, and thermal properties are yet to be experimentally and theoretically characterized, and further studies may project its maximum potential. Some of these studies have shown, for example, that silicene and germanene do not have a natural bandgap[4].

Phosphorene has been shown to have a bandgap from 0.3-2 eV [5], mobilities ranging higher than the average from 200 – 1000cm$^2$/Vs[6, 7] and an effective mass along the zigzag direction ten times larger than those in the armchair direction. Therefore, The study of its electronic,
electrical, optical, and phonon properties[7, 8] has been increased in the last years. In this work, we investigated the effect of disorder on the anisotropy in the effective mass[9].

2. Numerical model
Phosphorene has a crystalline structure as displayed in Figure 1(a)-(b). As opposed to graphene, phosphorene is non-planar layer, it forms a puckered layer in which phosphorus atoms are located on two parallel planes. Therefore, phosphorene has an anisotropic crystal structure, where \(a=3.314\) Å, \(c=4.376\) Å, and \(b=10.48\) Å, are the corresponding lattice constants in \(y\) (zigzag), \(x\) (armchair) and \(z\) directions.

We include the \(3s\) and \(3p_{x,y,z}\) electrons in the partially filled atomic shells and we take into account up to eighth nearest neighbor couplings through \(4\times4\) matrices referred to as \(\mathbf{T}\), with base of atomic shells. Here, the index \(m\) represents the \(s\), \(p_x\), \(p_y\), and \(p_z\) orbitals. The inter-atomic matrix elements \(T_{m,m'}(k)\) are given as the block sum of the wave functions of the \(s\) and \(p\) orbitals as shown in Equation 1,

\[
T^i_{m,m'} = t^i_{mm'} \sum_j e^{i\mathbf{d}_i \cdot \mathbf{k}}.
\]

Here, the 2D wave number is represented by \(\mathbf{k} = (k_x, k_y, 0)\). In this case, we sum only over the adjacent unit cells \(j\) which contains the atoms where the displacement vector magnitude is \(|\mathbf{d}_i|\). The hopping amplitudes \(t^i_{mm'}\) are initially written in terms of Slater-Koster parameters.

From the \(\mathbf{T}\), the Hamiltonian can be written as the following block matrix:

\[
H_{\text{mono}}(\mathbf{k}) = \begin{bmatrix}
T_0 + T_3 + T_8 & T_1 + T_4 & T_2^- + T_6^L + T_7^+ & T_5^- \\
T_1^T + T_4^T & T_0 + T_3 + T_8 & T_2^+ + T_6^R & T_5^- \\
T_2^- T_0^T + T_6^L + T_7^+ & T_0^T & T_1^T + T_4^T & T_2^+ + T_6^R + T_7^- \\
T_2^T + T_6^T + T_7^T & T_0^T & T_1^T + T_4^T & T_2^+ + T_6^R + T_7^- \\
\end{bmatrix}
\]

By diagonalizing \(H_{\text{mono}}(\mathbf{k})\), we obtained the band dispersion of monolayer phosphorene Figure 1(c).

We focus on coherent transport and hence compute \(G^r\), the retarded Green’s function between the electrodes via the recursive lattice Green’s function technique[10]. \(G^r\) can be found from \(G^r = [\mathbf{E}I - \mathbf{H} - \Sigma_\mathbf{S} - \Sigma_\mathbf{D}]^{-1}\). Here \(I\) is the identity matrix and \(\Sigma_\mathbf{S}, \Sigma_\mathbf{D}\) are the self-energies for Source (left) and Drain (Right) contacts, are calculated from the electrode’s Green’s function also obtained numerically using a recursive technique [11]. The Green’s function formalism has succeed in reproducing scanning probe microscopy experiments providing a framework to interpret the electronic properties as well as predicting new effects.

Coherent transport is studied within the Landauer-Büttiker formalism, which relates the conductance \(G(E)\) at a given energy \(E\) to the transmission function \(T(E)\) between the contacts as

\[
G(E) = G_0 T(E),
\]

with \(G_0 = \frac{2\pi^2 k_F^2}{\hbar}\). The transmittance \(T(E)\) is evaluated by means of the recursive Green’s function \(G^r\) using a two-terminal device configuration with contacts represented by the semi-infinite ideal phosphorene leads. A schematic representation is shown in Figure 2(a), where \(L\) is the number of slices and \(W\) is the typical number of sites in a given slice. \(T(E)\) can be evaluated by

\[
T(E) = \text{Tr} \left[ \Gamma_\mathbf{S} G^r \Gamma_\mathbf{D} (G^r)^\dagger \right].
\]
In these expressions $\Gamma_{S(D)} = i(\Sigma_{S(D)} - \Sigma_{S(D)}^\dagger)$ are the broadening function. The calculation of the resistance for each particular random distribution of disorder has been performed as the inverse of the differential conductance $R = \frac{1}{G} = \frac{R_0}{T}$, where $R_0 = 12.5\, \text{k}\Omega$.

In order to explore how the resistivity $R$ behaves as a function of disorder we fixed the local charge density $n$. $n$ could be evaluated as a function of the Fermi energy $E_F$ through

$$n = \frac{1}{A} \int_{\mu}^{E_F} dE \theta(E), \quad (5)$$

where $A = W \cdot L$ is the sheet area and $\mu$ denotes the local chemical potential. Note that in the conduction band, $E_F > \mu$ and therefore the integral is over positive energies ("electrons"), while in the valence band, $E_F < \mu$ and the integral is over negative energies ("holes"). $\theta$ is the global density of states (DOS), which can be readily obtained from the energy dependence of the scattering matrix.

3. Results and Discussion

3.1. Bands structure and effective mass

We obtained the band structure, the energy dispersions $E$, by diagonalizing the Tight Binding Hamiltonian Equation 1. In Figure 1(c), we displayed the Tight-Binding band structure for conduction band (CB) and valence band (VB) in zigzag and armchair directions (red point). We fit data to a quadratic curve ($E \approx aK^2$) to determine the effective mass of the valence and conduction bands in the armchair and zigzag directions.

The model is a good approximation around the high symmetry $\Gamma$-point. The effective mass, in CB (VB), along zigzag direction (corresponding to wavevector $k_y$), is flatter than in CB(VB) along the armchair direction. We can estimated the effective mass using the effective mass approximation $m^* = \frac{\hbar^2}{2E}$, then, we obtain $1.988m_e$, $3.4649m_e$, and $0.1665m_e$ for Conduction(valence) bands in zigzag and armchair directions respectively. There is an anisotropy
in the effective mass, the excitons in zigzag directions have an effective mass heavier than the excitons in armchair direction. This high anisotropic for both electron and hole carriers was observed in multi-layer phosphorene [12].

Figure 2. (a) Schematic representation of a phosphorene sample of length L and width W in the armchair and zigzag directions. The shadow areas represent the left and right semi-infinite contacts. (b) Average resistance as a function of length L for disorder case corresponding to a dense concentration of scatterers, with low disorder amplitudes ω. Continuous lines are linear fittings used to extract the resistivity in the diffusive regime of the data for each curve.

3.2. Disorder effect on mass-asymmetry

Charge density and substrate inhomogeneities can be modeled by adding a local disordered potential ω(r_i) to the orbital energy ε_iα in the lattice sites in the sample region. One of the simplest models for ω(r_i) is constructed as follows: We take N_{imp} random lattice sites R_k uniformly distributed as centers of Gaussian scatterers with a random amplitude ω_k taken from a uniform distribution over the interval (-t, t). This results in

$$\omega(r_i) = \sum_{k=1}^{N_{imp}} \omega_k e^{-|r_i - R_k|^2/2\xi^2}, \quad (6)$$

where ξ is the range of the potential. The concentration of scatterers is n_{imp} = N_{imp}/A, where A denotes the total area of the sample. Figure 2(a) is a schematic representation of the phosphorene of length L and wide W=60. The shadow areas represent the left and right semi-infinite contacts. Figure 2(b) shown the resistance (R) as a function of the system length L. The results correspond to the average over 300 disorder realizations for L ranging between 10 to 500, a concentration of scatterers is n_{imp} = 1% and range of the potential of ξ = 1.5. The colors represent different disordered potential ω and the dotted line gives the diffusive regime.

Once the hoppings have been characterized, we are interested in calculating the resistance along a more realistic phosphorene in which scatterers can be randomly distributed along and around the axis of the phosphorene. The calculation of the resistance (as the inverse of the differential conductance) for each particular random distribution of defects has been performed for each particular distribution of disorder.

In Figure 2(b) we plot the average resistance for a charge density and a concentration scatterers defined in all cases as ξ = 1.5. the bottom panel and top panel corresponding to resistance at conduction and valence band, respectively, around the γ point. Curves with the
same color in left (armchair) and right (zigzag) plots correspond to the same gaussian potential amplitude $U$. The range of potential is defined as $\xi$.

![Diagram](image)

**Figure 3.** (a) Resistivity as a function of disorder amplitudes $\omega$, showing a quadratic dependence. (b) shows the ratio between the averaged resistance in ZZ and AC direction for different ranges of gaussian potentials.

At zero temperature, the resistance for each defect realization strongly fluctuates along the nanoribbon length, showing the characteristic behavior of the disordered 1D system. The average resistance, however, presents a clear linear behavior until $L = 200$ for armchair direction and $L = 100$ for zigzag direction. For long systems the average resistance shows an exponential behavior as a function of the length, increasing the resistance fluctuations which is a typical feature of strongly localized systems. For both conduction and valence region, we have found the strongly localized regime and the exponential increase of the resistance as a function of the tube length. In the diffusive regime, we can then fit the resistance as a linear function of $L$ for every $\omega$. Here, the resistance would be given by $R = \rho L/A$, where the resistivity $\rho$ is a material parameter independent of the sample dimensions.

In Figure 3(a) are showing the resistivity as function de gaussian amplitude potential $\omega$. For each case we found that the resistivity depend, from comparison with Drude model, as $\rho = m \ast \omega^2/\eta q^2$. Then, we can obtained the anisotropic factor as $\rho_{ZZ}/\rho_{AC} = m_{ZZ}^*/m_{AC}^*$. Figure 3(b) shows the ratio between the averaged resistance in ZZ and AC direction for different range of gaussian potential. It is reasonable to expect the resistivity to be anisotropic as well, considering the anisotropy in the effective masses. In Figure 3(b) we computed the anisotropic factor as $\rho_{ZZ}/\rho_{AC} = m_{ZZ}^*/m_{AC}^*$. In the concentrated regime, $\xi \approx 1$, the anisotropics value for resistivity are $\rho_{ZZ}/\rho_{AC} = 39.4 \pm 0.5$ for conductance bands at $\omega = 1$. This is quantitatively similar to our estimates of anisotropy from bands structures, but quantitatively different from
results in the literature[13]. In the dilute regime, $\xi \gg 6$, the anisotropy value for resistivity are $\rho_{ZZ}/\rho_{AC} = 0 \pm 0.5$ for conductance band. Although the phosphorene is rather sensitive to environmental influence the measured ratio of $\rho_y/\rho_x$, the anisotropy is a effect to be consider in the design of the devices beacause is robust to the presence of disorder and can be increased.

4. Conclusion
We used a heuristic tight-binding model to obtain the electronic band structure of phosphorene around the high symmetry Γ-point. We fit data to a quadratic curve, from the effective mass approximation, we found that the effective mass in the zigzag direction is ten times greater than that in the armchair direction.

The anisotropy can be further identified directly from the anisotropic effective masses and Fermi velocities. The Fermi velocity and effective mass are calculated from the energy band structure directly. Here. The velocity of an electron (hole) along the armchair direction is much larger than the value along the zigzag direction.

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