External Strain Induced Semi-metallic and Metallic Phase of Chlorographene

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In order to overcome the limitations of graphene due to lack of intrinsic bandgap, it is generally functionalized with hydrogen or halogen atoms like fluorine and chlorine. Generally, such functionalization yields a moderate to high bandgap material in case of 100% coverage, for example ≈ 1.5 eV in graphene functionalized with chlorine atoms or chlorographene. In this paper, using ab initio calculations, we report very interesting transformations observed in chlorographene under external strain, driving it to a state with nearly vanishing bandgap (under tensile strain) and even converting it to a metal (under compressive strain). We also show the importance of spin-orbit coupling, responsible for the few meV bandgap of chlorographene observed under high tensile strain, which would have been a gapless semi-metal otherwise.

The past decade has seen a tremendous growth of two dimensional (2D) materials, with numerous discoveries of atomically thin layers with fascinating properties suitable for applications in next generation electronic, optoelectronic and magnetic devices.$^1$ The rise of 2D materials started with the first successful isolation of a single layer of graphite, known as graphene.$^2$–$^4$ Post-discovery, graphene enthralled the researches with it’s fascinating electronic-transport properties like quantum Hall Effect at room temperature, very high carrier mobility, long mean free path and ballistic transport of electrons.$^4$ In addition to this, superior mechanical strength, high thermal conductivity and remarkable flexibility of graphene makes it an ideal candidate for device applications.

The origin of exotic electronic-transport properties of graphene lies in it’s linear energy dispersion (resembling the Dirac spectrum of massless fermions) at the high-symmetry points located at the six corners (denoted as K points) of the hexagonal Brillouin zone.$^5$–$^6$ Since the highest occupied and lowest unoccupied band touches each other at the Dirac points (K points), graphene is classified as a semi-metal. Unfortunately, lack of intrinsic bandgap limits the use of graphene to some extent. For example, the advantage of ultrahigh electron mobility is nullified by high off current in graphene based field effect transistor (FET) devices.

Fabrication of nanoribbons and quantum dots is one possible solution, as bandgap appears due to quantum confinement effect.$^7$ Although graphene nanoribbons have several interesting features, like spontaneous spin polarization along the edges, their fabrication with atomically controlled edge shapes remains a challenge.$^8$–$^{10}$ Other alternative is to functionalize graphene via chemical adsorption of hydrogen$^{11,12}$ or halogen atoms like fluorine$^{13}$–$^{16}$ and chlorine.$^{17,18}$ Unfortunately, this leads to a large bandgap of magnitude 3.5–3.7 eV in case of hydrogenation, 2.9–3.1 eV in case of fluorination and 1.2–1.5 eV in case of chlorination, as reported in several computational and experimental studies.$^{11}$–$^{19}$ Reducing the bandgap is certainly going to make them more appealing for device applications.

Being atomically thin, 2D materials can not screen the external fields very effectively. As a result, perturbations like applied strain and electric field are known to significantly change the electronic band structure of 2D materials. For example, in case of MoS$_2$, experimental studies have reported nearly 100 meV bandgap decrease per percent of applied strain, accompanied by direct-to-indirect transition of the character of the bandgap.$^{20,21}$ Similar predictions have been made for 2D phosphorus allotropes, where applied strain is also found to switch the preferred conduction direction.$^{22}$–$^{24}$ Bandgap can also be tuned by applying an electric field in a direction perpendicular to the plane of the 2D material, as shown for MoS$_2$,$^{25}$–$^{27}$ phosphorene$^{28}$–$^{31}$ and multilayer graphene.$^{32}$

In this paper we select chlorographene, which has the lowest bandgap among the functionalized graphene siblings and study the effect of strain (within the elastic limit) on its electronic band structure. We show that, sizeable bandgap of chlorographene can be reduced to a vanishingly small value of a few meV (under tensile strain) and it can even be converted to a metallic state (under compressive strain). We find that spin-orbit coupling is responsible for the few meV bandgap observed under high tensile strain, otherwise which appears like a gapless semi-metallic state of chlorographene. Based on symmetry arguments, we expect the results to be qualitatively true for other materials with same space group symmetry and in that sense, our study is quite general in nature.

Structural optimizations and electronic band structure calculations are carried out using QUANTUM ESPRESSO$^{15}$ package, implementing density functional theory (DFT) using a plane-wave basis set (kinetic energy cutoff taken to be 80 Ry). Core electrons are treated using the norm-conserving pseudopotentials and exchange-correlation effects are included within the framework of generalized gradient approximations(GGA). A $k$–point mesh of $24 \times 24 \times 1$ is used to obtain the electron density in a self-consistent manner. Structural optimizations are carried out until the energy difference between two successive steps are less than $10^{-3}$ Ry and all three components of the force on each atom are less than $10^{-3}$ Ry/Bohr.
Graphene has a honeycomb lattice of carbon atoms with a space group symmetry of P6/mmm (\#191), which is lowered to P3m1 (\#164) by full chlorination (one Cl atom per C) and the resulting 2D material is known as chlorographene. The crystal structure and hexagonal unit cell of chlorographene is illustrated in Fig 1(a)-(b). Using the computational parameters mentioned above, the lattice constant of fully relaxed structure of chlorographene is measured to be 2.91 Å, while the C-C and C-Cl bond length is found to be 1.75 Å and 1.74 Å, respectively and the C-C-C and C-Cl bond angle is obtained to be 111.98° and 106.83°, respectively. The first Brillouin zone of chlorographene is shown in Fig 1(c) and the high symmetry points are marked as Γ (center of the Brillouin zone), K (corner of the Brillouin zone) and M (center of the edges of the Brillouin zone).

The electronic band structure is plotted along the high symmetry lines Γ-K, K-M and M-Γ [see Fig. 1(d)-(e)]. As shown in the diagram, a direct bandgap at the Γ point, measuring 1.5 eV, is obtained in case of chlorographene, which is in good agreement with the value reported in the literature. It is observed that the valence band maximum (VBM) is two fold degenerate (heavy hole and light hole), while the conduction band minimum (CBM) is non-degenerate. Degeneracy of the hole bands at the Γ point is dictated by symmetry and it is also observed in other 2D materials of P3m1 space group, like monolayer β phosphorus and arsenic, as well as blue phosphorous oxide. Two states at the VBM (one state at the CBM) corresponds to the irreducible representation E_u (A_{1g}) of D_{3d} point group. VBM (E_u) is found to be doubly degenerate.

Impact of deformation on electronic band structure is investigated by applying compressive (upto 7%) and tensile (upto 13%) strain bi-axially, such that the symmetry of the pristine material is preserved after contraction or expansion of the unit cell vectors. The strains applied are within the elastic limit predicted for chlorographene, as predicted by ab initio calculations. Bi-axial strain upto 6% has so far been reported experimentally in similar 2D materials like MoS_2. The overall effect of bi-axial strain is summarized in a three dimensional electronic band structure diagram, where only three low energy bands near the valence and conduction band edge of chlorographene are shown for the sake of clarity [see Fig. 2]. In this diagram, we plot the energy level shift (measured with respect to the vacuum energy level) of E_u and A_{1g} states, as a function of applied strain. Clearly, energy level of doubly degenerate E_u states falls with increasing tensile strain, while it rises with increasing compressive strain. In contrast, energy level of A_{1g} states falls with increasing tensile, as well as compressive strain. Due to the energy level shift of E_u and A_{1g} states, bandgap of chlorographene gradually closes with increasing strain, which finally leads to a phase transition. Shaded areas, located extreme right and left of Fig. 2, mark the regions where chlorographene is no longer a semiconductor. Interestingly, phase transition under tensile strain is qualitatively different from what we observe with compressive strain. It is found that, while a semiconductor to semi-metal transition takes place in the tensile region (beyond 12% strain), on the other hand, chlorographene transforms to a metallic state under compression (beyond 6.2% strain). Interestingly, two bands are also found to be touching each other along a circular line surrounding the Γ point in the latter state.

Let us first have a detailed discussion on what happens until the point of phase transition. As long as chlorographene exists as a semiconductor, doubly degenerate E_u states remain at the valence band top, while A_{1g} state prevails at the conduction band bottom. The orbital resolved band structure of chlorographene under tensile strain is shown in Fig 3 (a) and (b). Clearly, near...
FIG. 2. Effect of strain on band edges of chlorographene is shown. Energy level (measured with respect to the vacuum energy level) of the valence band edge ($E_u$) irreducible representation of $D_{3d}$ point group at the $\Gamma$ point) falls with increasing tensile strain, while it rises with increasing compressive strain. On the other hand, energy level of the conduction band edge ($A_{1g}$ irreducible representation of $D_{3d}$ point group at the $\Gamma$ point) falls with increasing tensile, as well as compressive strain. As a result of band edge shifting, bandgap of chlorographene closes gradually with increasing strain, followed by a phase transition (shaded region), which is qualitatively different for tensile and compressive strain. In the tensile side, a semiconductor to metal phase transition is found beyond 12% critical strain, while a semiconductor to metal phase transition is found beyond 6.2% compressive strain.

FIG. 3. Orbital resolved band structure of chlorographene is illustrated; under (a)-(b) tensile (0, 5 and 11%) and (c)-(d) compressive (0, 3 and 6%) strain. The corresponding atomic orbitals are mentioned in respective panels. (e) Weight of the atomic orbitals of Cl is found near the conduction band edge. However, contribution from $p_z$ orbital of Cl atom falls rapidly under tensile strain. Other than that, $p_z$ orbital of C has a significant weight in case of CBM of chlorographene, both under compression and tension. A summary of relevant atomic orbitals is given in Fig 3 (e) by plotting their weight as a function of strain. Clearly, in equilibrium (zero strain) weight of the atomic orbitals at the CBM is in the following order: $C_pz > Cl_z > Cl_p$. However, contribution from $s$ orbital of C atom rises and $p_z$ orbital of Cl atom falls rapidly under tensile strain. This is exactly opposite to what happens under compressive strain, where weight of $p_z$ orbital of Cl atom rises to prominence, while it decays to negligible values for $s$ orbital of C atom. The electronic band structures presented in Fig. 3 also clearly illustrates that the bandgap decreases with increasing strain (both compressive and tensile) and it’s magnitude is plotted as a function of strain in panel (f) of the same figure. Note that, the bandgap changes more sharply under compressive strain, although ultimately it drops to zero in either case and the particular nature of the phase transition is going to be discussed in the following paragraphs.

First, let us focus on the semi-metallic phase appearing beyond 12% tensile strain. A representative electronic band structure of semi-metallic phase of chlorographene (under 13% tensile strain) is shown in Fig. 4. Clearly, the valence band top and conduction band bottom is touching each other at the $\Gamma$ point. This originates from the two fold degeneracy of the $E_u$ states at the $\Gamma$ point. As discussed previously, $E_u$ states are doubly degenerate in
equilibrium (zero strain) also. It is not surprising that the degeneracy survives, because uniform biaxial strain does not change the symmetry of chlorographene. As shown in Fig. 4, energy level of \( E_u \) is higher than that of \( A_{1g} \) states, which is exactly opposite to what is observed in semiconducting state of chlorographene, i.e., in equilibrium (zero strain) and all the way to 12% tensile strain. At this critical value of strain, \( A_{1g} \) state drops below the energy level of \( E_u \) states, which marks the onset of semi-metallic state of chlorographene [also see Fig. 2]. Note that, in-between the semiconducting and semi-metallic phase, there might exist a triply degenerate state (two \( E_u \) and one \( A_{1g} \) state at the same energy level) at some particular value of strain, although it is difficult to identify because DFT can not accurately predict bandgap smaller than a few milli-electron volt. On the other hand, semi-metallic state beyond 12% strain is very robust because it originates from the two fold degeneracy of the \( E_u \) states, protected by the symmetry of chlorographene. Based on the orbital resolved band structure shown in Fig. 4, it is also clear that the \( E_u \) (\( A_{1g} \)) states at the \( \Gamma \) point are mainly composed of \( p_x \) and \( p_y \) orbital of Cl (\( s \) and \( p_z \) orbital of C), which is consistent with the trend observed for chlorographene under tensile strain [see Fig. 5(e)].

Finally, we discuss the phase transition under compression and as mentioned previously, it is qualitatively different from the transition taking place under tensile strain [also see Fig. 2]. Finer details are illustrated in Fig. 5(a) and (b), where electronic bands of chlorographene under 7% compressive strain are plotted along various high symmetry lines. Again, since uniform biaxial strain preserves the symmetries of chlorographene crystal, the doubly degenerate \( E_u \) states at the \( \Gamma \) point persists and have higher energy than that of \( A_{1g} \) states. Thus, similar to tensile strain, phase transition under compression also happens as the energy of \( A_{1g} \) drops below that of \( E_u \) states [see Fig. 2]. Orbital resolved band structure shown in Fig. 5(a) and (b) also reveals that the \( E_u \) (\( A_{1g} \)) states at the \( \Gamma \) point are mainly composed of \( p_x \) and \( p_y \) orbital of Cl (\( p_z \) orbital of Cl and \( p_z \) orbital of C), which is consistent with the trend observed for chlorographene under compressive strain [see Fig. 3(e)]. Note that, neither \( E_u \), nor \( A_{1g} \) states at the \( \Gamma \) point are at the Fermi level, which lies in between the two [see Fig. 5(a) and (b)]. This leads to a partially filled band and consequently chlorographene transforms from semiconducting to a metallic state. Note that, Fermi level crosses the energy bands in two distinct places between \( \Gamma M \), as well as \( \Gamma K \) [see insets of Fig. 5(a) and (b)]. This is further elucidated by using surface plots of \( E_1(k_x, k_y) \) and \( E_2(k_x, k_y) \), where \( E_2 \geq E_1 \) at a reciprocal lattice point \( (k_x, k_y) \). Since \( E_1 \) and \( E_2 \) are calculated with respect to the \( E_F \), Fermi level lies along the zero energy contour lines, illustrated by the blue and red circle. Two bands cross along the outer blue circle, as shown in panel (c) and (d). The inner red circle of panel (c) is the other zero energy contour line, related to the partially filled band of chlorographene.

So far our calculations do not include the effect of spin-orbit coupling. This is known to lift the degeneracy and induce energy gaps, especially at the high-symmetry points, in other 2D material like graphene.\(^{39}\) As discussed previously, the two \( p \) orbitals of Cl, which makes the VBM of chlorographene (when it is a semiconductor), are degenerate at the \( \Gamma \) point [see Fig 1 and Fig 3]. However, once the spin-orbit coupling\(^{40}\) is turned on, the degeneracy of the \( E_u \) states is lifted at the \( \Gamma \) point and the energy levels are split by a small margin of 20–40 meV. This is observed irrespective of the magnitude of the ap-
FIG. 6. Effect of spin-orbit coupling (SOC) on electronic band structure of chlorographene is shown for (a) 11% tensile, (b) 13% tensile and (c) 7% compressive strain. Clearly, degeneracy of the $E_u$ states at the $\Gamma$ point is lifted and a gap of magnitude 20 and 40 meV is created, in case of tensile and compressive strain, respectively. Additionally, in case of chlorographene under 7% compressive strain, a 10 meV energy gap is opened along the outer blue circle, where two bands were touching each other [see Fig. 5]. In panel (a) and (b), parities of the Bloch states at the $\Gamma$ point are labeled by + and -.

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Point group symmetry of the wave vector $k$ at the $\Gamma$, $K$ and $M$ point is $D_{3d}$, $D_3$ and $C_{2h}$, respectively and along the $\Gamma$-$K$, $K$-$M$ and $M$-$\Gamma$ line is $C_2$, $C_2$ and $C_s$, respectively.

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