Two-dimensional phosphorus carbide: Competition between $sp^2$ and $sp^3$ bonding

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Abstract

We propose previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer. Different stable geometries, which result from the competition between $sp^2$ bonding found in graphitic C and $sp^3$ bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. Depending on the category, we identify 2D-PC structures that can be metallic, semimetallic with an anisotropic Dirac cone, or direct-gap semiconductors with their gap tunable by in-layer strain.

There is growing interest in 2D semiconductors, both fundamental and as potential components in flexible, low-power electronic circuitry. A large number of substances with unique advantages and limitations has been studied in this respect, but consensus has not been reached regarding the optimum candidate. Semi-metallic graphene with an excellent carrier mobility has received the most attention so far, but all attempts to open up a sizeable, robust, and reproducible band gap have failed due to the negative side effects of the different modifications. Transition metal dichalcogenides (TMDs) such as MoS$_2$ or TcS$_2$ do have a sizeable fundamental band gap, but a lower carrier mobility. Recently isolated few-layer films of black phosphorus, including phosphorene monolayers, combine high carrier mobility with a sizeable and tunable fundamental band gap, but have limited stability in air.

Since both elemental carbon and phosphorus form stable 2D monolayers, which have been studied extensively, it is intriguing to find out, whether the compound phosphorus carbide (PC), also called carbon phosphide, may also be stable as a monolayer and display properties that may even be superior to both constituents. The plausibility of a 2D structure of PC derives from the same three-fold coordination found both in graphene and phosphorene. On the other hand, the 2D structure will likely suffer from a competition between the planar $sp^2$ bonding characteristic of graphene and the significantly different nonplanar $sp^3$ bonding found in phosphorene. The postulated 2D structure of PC with 1:1 stoichiometry is fundamentally different from the amorphous structure observed in deposited thin solid films, the postulated foam-like 3D structure, or the postulated GaSe-like multi-layer structures of PC containing C and P with the same $sp^3$ hybridization. On the other hand, 2D allotropes of PC are somehow related to postulated and partly to observed fullerene-like structures of CP$_x$, and to g-C$_3$N$_4$, called graphitic carbon nitride.
Figure 1: (Color online) Possible stable structures of an atomically thin PC monolayer, represented by (a-c) a tiling pattern and (d-i) by ball-and-stick models in both top and side view. The number of like nearest neighbors defines the structural category $N$. There are two stable allotropes, $\alpha$ and $\beta$, for each $N$. The primitive unit cells are highlighted and the lattice vectors are shown by red arrows. Two inequivalent P sites are distinguished by a subscript in (d).

In this Letter, based on $ab$ initio density functional calculations, we propose previously unknown allotropes of phosphorus carbide in the stable shape of an atomically thin layer. We find that different stable geometries, which result from the competition between $sp^2$ bonding found in graphitic C and $sp^3$ bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. We introduce the structural category $N$, defined by the number of like nearest neighbors, and find that $N$ correlates with the stability and the electronic structure characteristic. Depending on the category, we identify 2D-PC structures that can be metallic, semimetallic with an anisotropic Dirac cone, or direct-gap semiconductors with their gap tunable by in-layer strain.

Results and Discussion

As mentioned above, all atoms in the 2D-PC allotropes are threefold coordinated, similar to the planar honeycomb lattice of graphene. Thus, the structure can be topologically mapped onto a 2D lattice with sites occupied either by P or C atoms. Bisecting all nearest-neighbor bonds by lines yields a 2D tiling pattern, where each triangular tile with a characteristic color represents either a P or a C atom. Next, we define a structural category $N$ for each allotrope, with $N$ given by the number of like nearest neighbors. For $N = 0$, none of the atoms are connected to any like neighbors. Each C or P atom has only one like (C or P) neighbor for $N = 1$, and two like neighbors for $N = 2$. There is no $N = 3$ structure, which would imply a pure carbon or phosphorus lattice. The tiling patterns for different 2D-PC allotropes are shown in Fig. 1(a)-1(c). A similar categorization scheme has been used previously to distinguish between
different allotropes of 2D phosphorene, where $N$ was the number of “like” neighbors either in the upper or lower position within the lattice.

Whereas the tiling pattern is useful for simple categorization, it does not provide information about the nontrivial optimum structure shown in Fig. 1(d)-1(i), which results from a competition between the favored planar $sp^2$ hybridization of C and non-planar $sp^3$ hybridization of P. The side view of structures displayed in Fig. 1 best illustrates that allotropes with the same value of $N$ may be structurally different. In analogy to the different postulated phosphorene allotropes, we distinguish $\alpha_N$, which display a black-P-like armchair structure in side view, from $\beta_N$ phases of PC, which display a blue-P-like (or grey-As-like) zigzag structure in side view, and use the index $N$ to identify the structural category.

We start our discussion with $N = 1$ allotropes $\alpha_1$-PC and $\beta_1$-PC, shown in the middle column in Fig. 1. According to the definition of $N$, each atom has one neighbor of the same species and two of different species, forming isolated P-P and C-C dimers, as seen in the tiling pattern and the atomic structures. As seen in Fig. 2(a), the chemical octet rule is satisfied both on C sites in the graphitic $sp^2$ configuration and on P sites, containing a lone electron pair, in $sp^3$ configuration, indicating stability. Both allotropes have rectangular unit cells consisting of distorted hexagons. The unit cell of $\alpha_1$-PC with 8 atoms is larger than that of $\beta_1$-PC with 4 atoms.

In $N = 2$ allotropes $\alpha_2$-PC and $\beta_2$-PC, shown in the right column of Fig. 1, each atom has two like neighbors and one unlike neighbor. In the side view, these allotropes look very similar to those of the $N = 1$ category. The main difference becomes apparent in the top view. Whereas $N = 1$ structures contain ethylene-like $C_2$ units that are interconnected by P$_2$ dimers, $N = 2$ systems contain contiguous trans-polyacetylene-like all-carbon chains that are separated by P-chains. Due to the difference between the locally planar $sp^2$ bonding of C atoms and locally non-planar $sp^3$ bonding of P atoms, and due to the difference between equilibrium C-C and P-P bond lengths, the hexagons found in $N = 1$ structures change to pentagon-heptagon pairs in the optimum $N = 2$ structure resembling pentheptite or haeckelite structures related to graphitic carbon. As seen in Fig. 2(b), similar to $N = 1$ structures, the chemical octet rule is satisfied on both C and P sites. The lattice of $\alpha_2$-PC and $\beta_2$-PC allotropes contains rectangular unit cells with sixteen atoms.

In 2D PC compounds of category $N = 0$, shown in the left column of Fig. 1, each atom is surrounded by three unlike neighbors. There is no bonding configuration that would satisfy the octet rules on all sites. The bonding configuration depicted in Fig. 2(c) satisfies the octet rule only at the C sites, whereas the configuration in Fig. 2(d) favors only the P sites. The bonding configuration depicted in Fig. 2(e) contains alternating P-C chains containing P sites with lone electron pairs and C atoms in $sp^2$ configuration, which satisfy the octet rule, and P-C chains that do not satisfy it. In whatever bonding arrangement, the bonding configuration in $N = 0$ structures is frustrated. As a consequence, the $\alpha_0$-PC structure converts spontaneously from an initial armchair configuration, similar to $\alpha_1$-PC and $\alpha_2$-PC, to the zigzag structure depicted in Fig. 1(d), with details about the structural transformation discussed in the Supporting Information. The final $\alpha_0$-PC structure with inequivalent P$_1$ and P$_2$ sites reflects the bonding configuration in Fig. 2(e) containing P$_1$ sites with lone electron pairs and P$_2$ sites with lone electrons. The $\beta_0$-PC structure, depicted in Fig. 1(g), remains locally stable in the electronic configuration shown in Fig. 2(d).

Structural characteristics and the binding energy
Table 1: Calculated properties of different 2D-PC allotropes. \(< E_{coh} >\) is the cohesive energy per “average” atom with respect to isolated atoms. \(< \Delta E >=< E_{coh} > - < E_{coh,max} >\) describes the relative stability of a system with respect to the most stable structure. \(|\vec{a}_1|\) and \(|\vec{a}_2|\) are the in-plane lattice constants defined in Fig. [1]. \(d_{P-P}, d_{P-C}\) and \(d_{C-C}\) are the equilibrium bond lengths between the respective species. In \(\alpha_0\)-PC, the P-1-C bonds differ from the P-2-C bonds in length.

| Structure | \(\alpha_0\)-PC | \(\beta_0\)-PC | \(\alpha_3\)-PC | \(\beta_1\)-PC | \(\alpha_2\)-PC | \(\beta_2\)-PC |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(< E_{coh} >\) (eV/atom) | 4.80 | 4.75 | 5.05 | 5.06 | 5.20 | 5.20 |
| \(< \Delta E >\) (eV/atom) | -0.40 | -0.45 | -0.15 | -0.14 | 0.00 | 0.00 |
| \(|\vec{a}_1|\) (Å) | 8.41 | 5.12 | 8.73 | 4.76 | 9.84 | 10.59 |
| \(|\vec{a}_2|\) (Å) | 2.94 | 2.95 | 2.95 | 2.95 | 5.11 | 5.11 |
| \(d_{P-P}\) (Å) | – | – | 2.36 | 2.36 | 2.29 | 2.29 |
| \(d_{P-C}\) (Å) | 1.86 (P₁) | 1.78 | 1.84 | 1.84 | 1.85 | 1.85 |
| \(d_{C-C}\) (Å) | – | – | 1.38 | 1.38 | 1.44 | 1.44 |

of the different allotropes are summarized in Table [1]. Our energy results are obtained using the DFT-PBE functional (including spin polarization where required), which is known to overbind to some degree. We define the cohesive energy per atom, \(< E_{coh} >\), by dividing the total atomization energy by the total number of atoms, irrespective of species. The energy values in the first rows indicate that for given \(N\), the \(\alpha\) and \(\beta\) phases are almost equally stable, confirming that categorizing structures by the number of like neighbors at any site makes sense in terms of stability. Clearly, \(N = 2\) systems are most stable, followed by \(N = 1\) and \(N = 0\) allotropes. In particular, the cohesive energy of \(N = 2\) monolayers exceed the 5.14 eV/atom value of the postulated GaSe-like PC multi-layer structures by 0.06 eV/atom.

The lower stability of \(N = 0\) systems has been anticipated above, since the octet rule can not be satisfied at all sites. We also note that the \(\alpha_0\) phase is slightly more stable than the \(\beta_0\) phase of PC. The stability advantage of \(\alpha_0\)-PC derives from the larger variational freedom within the unit cell, which allows to distinguish two different P sites (P₁ and P₂), as shown in Fig. [1](d) and Fig. [2](e). The \(\alpha_0\)-PC structure consists of P₁(sp³)-C(sp²) chains, which obey the octet rule and form stable ridges, alternating with P₂-C chains, which do not obey the octet rule and form terraces. Additional support for the plausibility of the bonding configuration depicted in Fig. [2] comes from the equilibrium bond lengths, which are listed in Table [1]. With the exception of \(N = 0\) structures, the bond lengths depend primarily on \(N\) and are rather insensitive to the phase (\(\alpha\) or \(\beta\)). For \(N = 1\) and \(N = 2\) structures, the C-C bond lengths lie close to the 1.42 Å value in sp² bonded graphite (or graphene) and the P-P bond lengths are close to the 2.26–2.29 Å range found in layered black phosphorus (or phosphorene).

As seen in Fig. [2](a) and [2](b), P and C atoms are connected by a single-bond with \(d_{P-C}\approx1.85\) Å in \(N = 1\) and \(N = 2\) category structures. As suggested above, the bonding is frustrated at least in parts of \(N = 0\) structures. In the significantly reconstructed \(\alpha_0\)-PC system, depicted in Fig. [1](d), we can distinguish P₁ sites at ridges from P₂ sites at terraces. The lengths of the three P-C bonds are very similar at each of the these P sites, but differ significantly between P₁ and P₂. At P₁ sites that satisfy the octet rule, as seen in Fig. [2](e), the P₁-C bond length of 1.86 Å is very similar to \(N = 1\) and \(N = 2\) structures. At P₂ sites, which do not satisfy the octet rule, the frustrated bonds are much shorter with \(d_{P-C} = 1.71\) Å. As seen in Fig. [1](g), there is no reconstruction in the \(\beta_0\)-PC structure. As seen in the corresponding Fig. [2](c) or [2](d), the octet rule is only satisfied at either the P or the C sites. The P-C bonds are frustrated and their length of 1.78 Å lies in-between the P₁-C and P₂-C bond lengths in \(\alpha_0\)-PC.

Results of our DFT-PBE electronic band structure calculations for monolayers of the six proposed PC allotropes are presented in Fig. [3].
Figure 3: (Color online) Electronic band structure, density of states (DOS), and charge density $\rho_{vc}$ associated with valence frontier states of $\alpha_N$ and $\beta_N$ allotropes, where $N$ is the structural category defined in the text and used in Fig. 1. The energy range associated with $\rho_{vc}$ is indicated by the green shaded region in the band structure and DOS panels and extends from $E_F - 0.45$ eV $< E < E_F$ for semiconducting $\alpha_0$-PC in (a), from $E_F - 0.40$ eV $< E < E_F$ for semiconducting $\alpha_1$-PC in (c) and $\beta_1$-PC in (d), and from $E_F - 0.10$ eV $< E < E_F$ for metallic $\beta_0$-PC in (b), and for semi-metallic $\alpha_2$-PC in (e) and $\beta_2$-PC in (f). For each system, isosurface plots of $\rho_{vc}$ are displayed in the right-side panels and superposed with ball-and-stick models of the structure in top and side view. The isosurface values of $\rho_{vc}$ are $1.0 \times 10^{-3}$ e/Å$^3$ in (a), $2.0 \times 10^{-3}$ e/Å$^3$ in (b), $0.5 \times 10^{-3}$ e/Å$^3$ in (c) and (d), and $0.5 \times 10^{-4}$ e/Å$^3$ in (e) and (f).

The electronic band structure and associated density of states (DOS) of $N = 0$ systems is shown in Fig. 3(a) and 3(b). Our results in Fig. 3(a) suggest that $\alpha_0$-PC is an indirect-gap semiconductor with a band gap of $\approx 0.7$ eV. In stark contrast, the structurally similar $\beta_0$-PC allotrope is metallic according to Fig. 3(b). As suggested earlier, all bonds and electronic configurations are frustrated in $\beta_0$-PC, with all C sites engaging only three valence electrons in $sp^2$-like bonds, leaving one lone electron behind, and the angle at the P ridge being too large for typical $sp^3$ bonding. This finding, in particular the presence of a non-bonding electron in the C2$\rho_\perp$ orbital, is seen in the frontier states of $\beta_0$-PC that are depicted in the right panel of Fig. 2(b).

$\alpha_0$-PC is quite different from $\beta_0$-PC, as it contains two inequivalent P and C sites. The $P_1$ site at the ridge displays the favored $sp^3$ bonding characteristic and its lone pair orbital is present in the frontier state displayed in the right-hand panel of Fig. 3(a). In contrast, the bonding is very different at the $P_2$ site, where the lone pair orbital does not contribute to the frontier state. The flat bonding geometry near this site is reminiscent of $sp^2$ bonding at the C sites. The added flexibility provided by a larger unit cell allows for additional stabilization of $\alpha_0$-PC due to the opening of a band gap, with vague analogy to the Peierls instability.

As seen in Fig. 3(c) and 3(d), both $\alpha_1$-PC and $\beta_1$-PC have a direct band gap, which we attribute to the presence of isolated ethylene-like units men-
Figure 4: (Color online) Effect of uniaxial in-layer strain on (a) the relative binding energy $\Delta E_{\text{tot}}$ and (b) the fundamental band gap in different PC allotropes. Results for $\alpha_0$-PC, $\beta_0$-PC, $\alpha_1$-PC, $\beta_1$-PC, $\alpha_2$-PC and $\beta_2$-PC are distinguished by color and symbols. Results for strain in the $x$-direction, defined in Fig. 1, are shown by solid lines and for strain in the $y$-direction by dashed lines.

According to Fig. 3(e) and 3(f), also the two $N = 2$ allotropes, $\alpha_2$-PC and $\beta_2$-PC, share very similar band structure, DOS and frontier orbitals due to structural similarities. The electronic structure of these systems is nevertheless very different from the other two categories, chiefly due to the presence of trans-polyacetylene-like chains mentioned above. Both $\alpha_2$-PC and $\beta_2$-PC display a Dirac cone at the Fermi level, at a crystal momentum between $\Gamma$ and $Y$. As mentioned before, the distinguishing feature of $N = 2$ structures is the alternation between chains consisting of pure P or pure C atoms. Fig. 2(b) indicates that all P sites have occupied lone pair orbitals, which are also reflected in the frontier states. The P chains form ridges within the structure, with bond angles characteristic of $sp^3$ bonding found in black phosphorus. The structure of the carbon chains, also illustrated in Fig. 2(b), resembles that of conjugated trans-polyacetylene or graphene with $sp^2$ bonding, and the presence of $C2p\perp$ orbitals in the frontier states is clearly seen in the right-side panels of Fig. 3(e) and 3(f). Differences between equilibrium bond length and bond angles of the P and C chains are accommodated by introducing pentagon-heptagon pairs. The conjugation within C chains and their suppressed dimerization caused by their bonding to adjacent P chains lies behind the formation of the Dirac cone. Due to the strong anisotropy in the system, caused by the direction of the trans-polyacetylene-like chains, the Dirac cone is anisotropic in the plane of the layer. We have found that uniaxial strain may be used to eliminate the anisotropy of the Dirac cone, but will also change the location of the Dirac point along the $\Gamma - Y$ line. More information about the Dirac cone is provided in the Supporting Information.

Even though DFT-PBE calculations notoriously underestimate the fundamental band gap between occupied and unoccupied states, the calculated dispersion $E(k)$ of individual bands is believed to closely resemble experimental values. For the sake of comparison, we have also performed DFT-HSE06 calculations with a hybrid exchange-correlation functional for the same structures. As seen in the Supporting Information, our DFT-PBE and DFT-HSE06 results are closely related. In particular, DFT-HSE06 opens the band gap in semiconducting $\alpha_0$-PC, $\alpha_1$-PC and $\beta_1$-PC structures,
but keeps the metallic character of $\beta_0$-PC and the semi-metallic character of $\alpha_2$-PC and $\beta_2$-PC.

Similar to other non-planar 2D systems like phosphorene, PC is susceptible to even minute in-plane stress, which can cause major distortions in the geometry, affecting the electronic structure and bonding. To quantify this effect, we have determined the effect of tensile and compressive strain on the stability and the fundamental band gap in the different PC allotropes and present the results in Fig. 4. We have considered uniaxial strain along the $x$- and the $y$-direction, defined in Fig. 1. Since all allotropes discussed here are non-planar, applying in-layer strain changes the effective thickness of the layers and vice versa. As expected, layer thickness is reduced under tensile strain and increased under compressive strain. For strain values below 5%, we have observed changes in layer thickness of up to 10%. The distinct structural anisotropy, best seen in the side views, translates into a distinct anisotropy of the strain energy with respect to the strain direction, shown in Fig. 4(a). Similar to black phosphorene, the system appears soft when strained along the $x$-direction normal to the ridges and valleys, whereas it is much stiffer when distorted along the $y$-direction. We find the $\alpha$ phase to be particularly soft in the $x$-direction, with compressive or tensile strain requiring $\Delta E \lesssim 5$ meV/atom in strain energy.

The dependence of the fundamental band gap on the in-layer strain, as obtained by our DFT-PBE calculations, is shown in Fig. 4(b). We find that compression along the soft $x$-direction does not affect the band gap much, quite unlike what is expected to occur in black phosphorene. This is quite different from our results for strain along the stiffer $y$-direction. There, we observe the fundamental band gap to disappear at compressive strain exceeding 4% for $\alpha_1$-PC and 3% for $\beta_1$-PC. We also find that the metallic character of $\beta_0$-PC and semi-metallic character of $\alpha_2$-PC and $\beta_2$-PC are not affected by tensile or compressive strains up to 5% applied along the $x$- or the $y$-direction. Since vertical strain causing a 10% reduction of the layer thickness is equivalent to an effective tensile in-layer strain below 5%, we can judge its effect on the electronic structure based on the above findings.

Even though the cohesive energy of the 2D structures presented here exceeds that of previously discussed PC systems, the calculated cohesive energy of per formula unit still falls 0.54 eV short of the sum of the cohesive energies of pure black phosphorene, 3.27 eV, and pure graphene, 7.67 eV. Even though the PC allotropes discussed here are all stable, as seen in the vibration spectra presented in the Supporting Information, the slight energetic preference for pure components in favor of the PC compound should offer challenges in the synthesis. We believe that recent advances in supramolecular assembly may solve this problem. Similar to our requirements, precisely designed structures including graphdiyne, graphene nanoribbons, and carbon nanotubes have been assembled using wet chemical processes from specific molecular precursors. In the same way, we expect that the postulated 2D-PC structures may be formed of proper molecular precursors that contain $sp^2$ bonded carbon and $sp^3$ bonded phosphorus.

**Conclusions**

In conclusion, we have performed *ab initio* density functional calculations and identified previously unknown allotropes of phosphorus carbide (PC) in the stable shape of an atomically thin layer. We found that different non-planar stable geometries, which result from the competition between $sp^2$ bonding found in graphitic C and $sp^3$ bonding found in black P, may be mapped onto 2D tiling patterns that simplify categorizing of the structures. We have introduced the structural category $N$, defined by the number of like nearest neighbors ranging from 0 to 2, and found that $N$ correlates with the stability and the electronic structure characteristic. We found structures of the $N = 0$ category to be either metallic, or to reconstruct spontaneously to a more stable structure with a larger unit cell and a sizeable fundamental gap. Systems of the $N = 1$ category are more stable than $N = 0$ systems, display a significant, direct band gap and a significant anisotropy of the effective mass of carriers. Category $N = 2$ systems are the most stable of all, are semi-metallic, and display an anisotropic Dirac cone at the Fermi level. Due to their non-planar character, all systems can sus-
tain in-layer strain at little energy cost. The fundamental band gap is not very sensitive to strain in most systems with the exception of \( N = 1 \) allotropes, where it closes upon applying compressive strain of \( \leq 5\% \) along the ridges and valleys.

Methods

We use \textit{ab initio} density functional theory (DFT) as implemented in the SIESTA\textsuperscript{32} code to obtain insight into the equilibrium structure, stability and electronic properties of 2D-PC allotropes reported in the main manuscript. Periodic boundary conditions are used throughout the study, with monolayers represented by a periodic array of slabs separated by a 15 Å thick vacuum region. We use the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{33} exchange-correlation functional, norm-conserving Troullier-Martins pseudopotentials,\textsuperscript{34} and a double-\( \zeta \) basis including polarization orbitals. The reciprocal space is sampled by a fine grid\textsuperscript{35} of \( 8 \times 12 \times 1 \) \( k \)-points in the Brillouin zone of the primitive unit cell of 4 atoms or its equivalent in supercells. SIESTA calculations use a mesh cutoff energy of 180 Ry to determine the self-consistent charge density, which provides us with a precision in total energy of \( \leq 2 \) meV/atom. All geometries have been optimized using the conjugate gradient method,\textsuperscript{36} until none of the residual Hellmann-Feynman forces exceeded \( 10^{-2} \) eV/Å. Since the fundamental band gap is usually underestimated in DFT-PBE calculations, we have resorted to the HSE06\textsuperscript{26,27} hybrid exchange-correlation functional, as implemented in the VASP\textsuperscript{37–40} code, to get a different (possibly superior) description of the band structure. We use 500 eV as energy cutoff and the default mixing parameter value \( \alpha = 0.25 \) in these studies. DFT-PBE and DFT-HSE06 band structure results are compared in the Supporting Information.

Supporting Information Available: The geometry transformation pathway and corresponding changes in the electronic band structure of \( \alpha_0 \)-PC, details of the electronic band structure in all PC allotropes, and the phonon band structure of \( \beta_0 \)-PC and \( \beta_1 \)-PC. This material is available free of charge via the Internet at [http://pubs.acs.org/](http://pubs.acs.org/).

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Notes

The authors declare no competing financial interest.

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