Low-symmetry two-dimensional BNP$_2$ and C$_2$SiS structures with high and anisotropic carrier mobilities

Shixin Song,$^1$ Jie Guan,$^1$,* and David Tománek$^{2,†}$

$^1$School of Physics, Southeast University, Nanjing, 211189, PRC
$^2$Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824, USA

We study the stability and electronic structure of previously unexplored two-dimensional (2D) ternary compounds BNP$_2$ and C$_2$SiS. Using ab initio density functional theory, we have identified four stable allotropes of each ternary compound and confirmed their stability by calculated phonon spectra and molecular dynamics simulations. Whereas all BNP$_2$ allotropes are semiconducting, we find C$_2$SiS, depending on the allotrope, to be semiconducting or semimetallic. The fundamental band gaps of the semiconducting allotropes we study range from 1.4 eV to 2.2 eV at the HSE06 level and display carrier mobilities as high as $1.5\times10^5$ cm$^2$/V$\cdot$s$^{-1}$. Such high mobilities are quite uncommon in semiconductors with so wide band gaps. Structural ridges in the geometry of all allotropes cause a high anisotropy in their mechanical and transport properties, promising a wide range of applications in electronics and optoelectronics.

INTRODUCTION

Two-dimensional (2D) materials have intrigued researchers around the world since the successful mechanical exfoliation of graphene [1]. Even though graphene remains unsurpassed in terms of high charge carrier mobility, the vanishing band gap in the pristine material precludes its use from semiconducting circuitry [2, 3]. Other 2D materials including transition metal dichalcogenides (TMDs) such as MoS$_2$ have sizable band gaps, but are not as useful due to their low carrier mobility [4, 5]. Phosphorene, a monolayer of black phosphorus, combines high and anisotropic carrier mobility with a sizeable and tunable band gap [6–8], but is unstable under ambient conditions [9]. In spite of significant efforts to improve the performance of 2D materials in semiconducting devices, the progress has been moderate. There is a need to find new 2D semiconductors with substantial band gaps and high carrier mobilities.

Phosphorus carbide (PC), a recently proposed 2D material, has been predicted to be stable [10] and to display promising electronic behavior including high carrier mobility [11]. Of the stable allotropes, the semiconducting α$_1$-PC phase, also called black phosphorus carbide (b-PC), has been successfully synthesized. It shows a high field-effect mobility $\mu = 1995$ cm$^2$/V$\cdot$s$^{-1}$ of holes at room temperature [12], good infrared response [13] and tunable anisotropic plasmonic performance [14]. The narrow band gap, however, limits the performance of PC-based field-effect transistors (FETs) due to a relatively low ON/OFF ratio [12]. Experimental data for 2D GeP [15], another low-symmetry IV-V compound with strongly anisotropic conductance, indicate a high field-effect ON/OFF ratio $\approx 1 \times 10^4$, but a low carrier mobility $\mu = 0.35$ cm$^2$/V$\cdot$s$^{-1}$. Theoretical explorations have been extended to other 2D IV-V compounds, which are not isoelectronic to PC. These include germanium triphosphide [16] GeP$_3$, tin triphosphide [17] SnP$_3$, and phosphorus hexacarbide [18] PC$_6$. However, all these systems have narrow band gaps similar to α$_1$-PC and share a hexagonal honeycomb lattice structure and thus a weak transport anisotropy. 2D structures with a substantial band gap, high carrier mobility and strong in-layer anisotropy are still missing.

In search of such 2D materials inspired by anisotropic 2D PC structures, we have applied an effective design strategy known as “isoelectronic substitution”. This process involves substituting certain elements in the structure by their neighbors in the periodic table, yet keeping the total valence electron count unchanged. This approach, which has been successfully applied in both 3D and 2D systems, allows to change physical and chemical properties of the system without drastically changing the structure. In this way, the diamond structure of bulk silicon with a diatomic unit cell can be changed to the isoelectronic Si$_3$AlP, when one Si atom is substituted by Al and the other by P in every other unit cell, thus significantly increasing light absorption in the visible region [19]. In semimetallic 2D graphene with a diatomic basis, substituting one C atom by B and the other by N forms the h-BN structure, a wide-gap insulator. In a similar way, substituting every other atom in phosphorene by Si and S atoms results in the 2D SiS structure [20, 21]. The same isoelectronic substitution in 2D group V systems leads to 2D group IV-VI compounds including GeS, GeSe, and SnS with a lower symmetry and a wide range of physical properties [22–25].

In this study, we propose isoelectronic substitution in 2D structures of phosphorus carbide that leads to previously unknown ternary compounds BNP$_2$ and C$_2$SiS. Our ab initio density functional calculations identify four stable allotropes of each compound that share the 2D geometry with PC. Calculated phonon spectra and ab initio molecular dynamics (MD) simulations confirm the stability of each of these allotropes. Due to structural ridges in the geometry, all allotropes considered exhibit a sig-
significant anisotropy in the elastic response. Electronic structure calculations indicate that \( \alpha_1 \) and \( \beta_1 \) phases of \( \text{C}_2\text{SiS} \), as well as all four \( \text{BNP}_2 \) allotropes, are semiconductors with a wide range of band gap values. Carrier mobility calculations show that most of the semiconducting allotropes exhibit high and strongly anisotropic carrier mobilities. The remaining \( \alpha_2-\text{C}_2\text{SiS} \) and \( \beta_2-\text{C}_2\text{SiS} \) allotropes were found to be semimetallic, displaying an elliptically distorted Dirac cone in their band structure caused by their structural anisotropy.

**COMPUTATIONAL TECHNIQUES**

We have used *ab initio* density functional theory (DFT), as implemented in the VASP code [26–28], throughout the study. We applied periodic boundary conditions, with 2D structures separated by a vacuum region in excess of 20 Å. The reciprocal space was sampled by a fine grid [29] of \( 8\times6\times1 \) \( k \)-points in the Brillouin zone of 8-atom unit cells or its equivalent in supercells. We used projector-augmented-wave (PAW) pseudopotentials [30] and the Perdew-Burke-Ernzerhof (PBE) [31] exchange-correlation functionals. Selective band structure calculations were performed using the hybrid HSE06 functional [32, 33] with the default mixing parameter \( \alpha = 0.25 \). We utilized the DFT-D2 [34] method to represent van der Waals (vdW) corrections to the total energy. We used a cutoff energy of 500 eV for the plane-wave basis set and considered the electronic structure to be converged once the total energy difference between subsequent electronic structure iterations would not exceed \( 10^{-5} \) eV. All geometries were optimized using the conjugate-gradient method [35], until none of the residual Hellmann-Feynman forces exceeded \( 10^{-2} \) eV/Å. The phonon calculations were carried out using the density functional perturbation theory [36–38], as implemented in the PHONOPY code [39]. The system dynamics was studied using canonical *ab initio* MD simulations with 3 fs time steps. Our results are for supercells containing more than 100 atoms, which were kept at temperatures of 300 K, 500 K or 1000 K for periods exceeding 15 ps.
whereas B and N atoms prefer the sp\(^2\) configuration with a lone electron pair, whereas B and N atoms prefer the sp\(^2\) configuration in all BNP\(_2\) allotropes. The \(\alpha_1\) and \(\beta_1\) allotropes represent two equivalent ways to achieve optimum configuration with the same topology, in analogy to black and blue phosphorene. [40]

The \(\alpha_2\) and \(\beta_2\) allotropes of BNP\(_2\) contain alternating chains of P and BN along the \(y\)-direction. The mismatch between the equilibrium P-P and B-N bond lengths leads to the formation of pentagon-heptagon pairs instead of hexagons.

The structure of all 2D allotropes of C\(_2\)SiS closely resembles that of BNP\(_2\) due to the coexistence of sp\(^2\)-bonded C atoms and sp\(^3\)-bonded Si and S atoms. Similar to BNP\(_2\), the \(\alpha_1\) and \(\beta_1\) allotropes of C\(_2\)SiS contain isolated Si-S and C-C dimers. Also in this case, there are two distinguishable, topologically equivalent geometries. Even though the polar Si-S bonds are out of plane in this compound, their alternating orientation eliminates a net dipole moment.

A summary of the structural characteristics and the cohesive energy of all these allotropes is presented in Table I. In the BNP\(_2\) system, the B-N dimers in \(\alpha_1\) and \(\beta_1\) allotropes are connected by typical double bonds with

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**RESULTS AND DISCUSSION**

**Structure of BNP\(_2\) and C\(_2\)SiS 2D allotropes**

As introduced above, the 2D compounds BNP\(_2\) and C\(_2\)SiS are isoelectronic to previously reported PC monolayer structures [10]. We have identified four 2D allotropes, called \(\alpha_1\), \(\beta_1\), \(\alpha_2\) and \(\beta_2\), for each of the systems. The most stable structures of each allotrope are shown in Fig. 1. All atoms are 3-fold coordinated, causing a coexistence of sp\(^2\) and sp\(^3\) bonding and leading to structural ridges in the geometry of all allotropes. When viewed from the side, the \(\alpha\) allotropes have an armchair profile, whereas the \(\beta\) allotropes have a zigzag profile. With the exception of \(\beta_1\)-C\(_2\)SiS with 8 atoms in the unit cell, all allotropes have rectangular unit cells containing 16 atoms. Additional metastable structures with different atomic arrangements in the unit cell are discussed in the Appendix.

As seen in Fig. 1, the optimized \(\alpha_1\) and \(\beta_1\) allotropes of BNP\(_2\) structures consist of isolated P-P and B-N dimers forming a 2D hexagonal structure. Since the orientation of the B-N dimers alternates in the plane of the system, there is no net dipole moment in the system. P atoms prefer the sp\(^3\) configuration with a lone electron pair, whereas B and N atoms prefer the sp\(^2\) configuration in

| TABLE I. Calculated equilibrium properties of BNP\(_2\) and C\(_2\)SiS 2D allotropes. |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| &gt;1 | &lt;9 | &lt;5 | &lt;4 | &lt;11 | &lt;5 | &lt;4 | &lt;11 | &lt;5 |
| | \(\alpha_1\) | \(\beta_1\) | \(\alpha_2\) | \(\beta_2\) | \(\alpha_1\) | \(\beta_1\) | \(\alpha_2\) | \(\beta_2\) |
| d\(_{PN}\) (Å)\(^b\) | 2.25 | 2.25 | 2.27\(^h\) | 2.27\(^h\) |
| d\(_{PN}\) (Å)\(^b\) | 1.78 | 1.78 | 1.79 | 1.79 |
| d\(_{PN}\) (Å)\(^b\) | 1.94 | 1.94 | 1.95 | 1.95 |
| d\(_{PN}\) (Å)\(^b\) | 1.40 | 1.40 | 1.46 | 1.46 |
| d\(_{Si-S}\) (Å)\(^b\) | 2.49 | 2.46 | 2.41\(^h\) | 2.40\(^h\) |
| d\(_{Si-S}\) (Å)\(^b\) | 1.77 | 1.77 | 1.77 | 1.77 |
| d\(_{Si-S}\) (Å)\(^b\) | 1.94 | 1.94 | 1.95 | 1.95 |
| d\(_{C-C}\) (Å)\(^b\) | 1.36 | 1.36 | 1.42 | 1.42 |
| \(E_{coh}\) (eV/atom)\(^a\) | 4.74 | 4.74 | 4.98 | 4.98 | 5.25 | 5.26 | 5.54 | 5.54 |
| \(E_{form}\) (eV/atom)\(^d\) | -0.01 | -0.01 | -0.25 | -0.24 | 0.68 | 0.68 | 0.39 | 0.39 |
| \(c_{11}\) (N/m)\(^f\) | 7.17 | 40.59 | 10.24 | 57.53 | 6.42 | 33.79 | 14.89 | 53.35 |
| \(c_{22}\) (N/m)\(^f\) | 156.02 | 144.13 | 189.59 | 173.68 | 145.94 | 124.02 | 199.72 | 185.35 |
| \(E_g-PBE\) (eV)\(^f\) | 0.52 | 0.80 | 1.39 | 1.26 | 0.71 | 0.70 | 0.00 | 0.00 |
| \(E_g-HSE06\) (eV)\(^g\) | 1.38 | 1.69 | 2.15 | 2.06 | 1.57 | 1.40 | 0.00 | 0.00 |

\(a\) \([\bar{a}_1]\) and \([\bar{a}_2]\) are the in-plane lattice constants defined in Fig. 1.

\(b\) \(d\) is the equilibrium bond length between the respective species.

\(c\) \(E_{coh}\) is the cohesive energy per average atom with respect to elemental structures.

\(d\) \(E_{form}\) is the formation energy per average atom with respect to elemental structures.

\(e\) \(c_{11}\) (\(c_{22}\)) are the 2D elastic constants along the \(x\) (\(y\)) direction.

\(f\) \(E_g-PBE\) is the band gap value at the DFT-PBE level.

\(g\) \(E_g-HSE06\) is the band gap value at the DFT-HSE06 level.

\(h\) Length of bonds within the structural plane.

\(^i\) Length of bonds out of the structural plane.
FIG. 3. Electronic structure of a BNP$_2$ monolayer. Shown are the calculated band structure $E(k)$ and the density of states (DOS) including its projection on individual atoms (left panels), the partial charge density distributions at the valence band maximum (VBM) and the conduction band minimum (CBM) (right panels) of the (a) $\alpha_1$, (b) $\alpha_2$, (c) $\beta_1$, and (d) $\beta_2$ allotropes. All results are based on the DFT-PBE functional with the exception of DFT-HSE06 data, which are shown by the red dashed lines in the band structure plots. The blue arrows indicate the fundamental band gap. Contributions of different atoms are distinguished by color in the PDOS plots. Isosurface plots of the partial charge density are presented at the isosurface value of $8.0 \times 10^{-3}$ $\text{e/Bohr}^3$ for all allotropes.

$d_{BN} \approx 1.40$ Å, close to the 1.403 Å value in amino borane [41]. The bond length of the B-N chains in $\alpha_2$ and $\beta_2$ allotropes is slightly longer, at about 1.46 Å, close to the 1.45 Å value in 2D $h$-BN [42]. These results are consistent with the $sp^2$ configuration of B and N atoms in 2D BNP$_2$.

We find similar structural characteristics in the C$_2$SiS$_2$ system. As expected for $sp^2$-bonded C atoms, the C-C bond lengths are comparable to the double bonds in ethylene and the conjugated bonds in benzene or graphene. The length of all the other single bonds appears rather insensitive to the structure.

It is also noteworthy that P-N bonds are slightly shorter than P-B bonds in BNP$_2$ due to the smaller atomic radius of the more electronegative element. The same is true, for the same reason, with the C-S bonds that are slightly shorter than C-Si bonds in C$_2$SiS$_2$ allotropes.

For the sake of easy comparison, we define the cohesive energy $E_{\text{coh}}$ of an “average” atom by dividing the total atomization energy by the total number of atoms. Our results for $E_{\text{coh}}$ are listed in Table I. We found that for both BNP$_2$ and C$_2$SiS$_2$, $\alpha$ and $\beta$ allotropes with the same index are almost equally stable. Our results also indicate that for both BNP$_2$ and C$_2$SiS$_2$, $\alpha_2$ and $\beta_2$ allotropes are energetically more stable than $\alpha_1$ and $\beta_1$ allotropes by $\Delta E_{\text{coh}} \approx 0.2 - 0.3$ eV/atom. We find the C$_2$SiS$_2$ structures to be generally more stable than BNP$_2$ structures. The listed values of $E_{\text{coh}} \approx 5$ eV/atom here are comparable to cohesive energies found in PC monolayers [10].

We have further confirmed the stability of each allotrope by calculating the phonon spectra and by performing ab initio MD simulations. Details of all these calculations are presented in the Appendix.

We also calculated the formation energy per ‘average atom’ $E_{\text{form}}$ to investigate the relative stability of the ternary allotropes comparing with respect to their elemental components. We defined $E_{\text{form}}$ as

$$E_{\text{form}}(X_1Y_mZ_n) = E(X_1Y_mZ_n) - \frac{l \cdot E(X) + m \cdot E(Y) + n \cdot E(Z)}{l + m + n},$$

where $E(X_1Y_mZ_n)$, $E(X)$, $E(Y)$, $E(Z)$ are the respective total energies per average atom of the $X_1Y_mZ_n$ compound and the elemental structures of X, Y and Z. In the particular case of 2D BNP$_2$ and C$_2$SiS$_2$ structures, the elemental structures we consider are bulk boron, gas of N$_2$ molecules, phosphorene, graphene, bulk silicon and bulk sulfur. The results of $E_{\text{form}}$ for all the allotropes are listed in Table I. $E_{\text{form}} > 0$ indicates instability and possibility of exothermic decomposition, whereas $E_{\text{form}} < 0$ indicates stability.

Our results for $E_{\text{form}}$ in Table I indicate that all BNP$_2$ allotropes are stable and will not decompose below $\approx 1000$ K, at which point bonds may be broken.
an important role in carrier mobilities. For the semiconducting allotropes, these values play differences \( \Delta E \) of magnitude smaller than cohesive energies and compressions, subjected to \( \leq 10\% \) compressive or tensile strain. The \( \Delta E \) values obtained using these calculations, are summarized in Table I. We should note here that the interpretation of cohesive energies as self-energies is strictly underestimated. We find this to be the case when comparing band gap values based on DFT-PBE and the hybrid DFT-HSE06 functional in Table I. As seen when comparing band structure results based on DFT-PBE, given by the solid lines in Fig. 3, and DFT-HSE06, shown by the red dashed lines, the main difference is the opening of the fundamental band gap in DFT-HSE06, whereas the band dispersion is unaffected. We also present the total electronic density of states (DOS) and its projection onto the different species next to the band structure plots.

Contour plots of the projected DOS (PDOS) of all BNP\(_2\) allotropes at the valence band maximum (VBM) and conduction band minimum (CBM) are shown in Fig. 3, with the contributions to VBM and CBM distinguished by color. We find the character of the VBM to be dominated by the lone-pair states of the sp\(^3\) hybridized P atoms in all BNP\(_2\) allotropes. The character of the CBM is very different. The dominant contribution in \( \alpha_1 \) and \( \beta_1 \) allotropes of BNP\(_2\) comes from out-of-plane \( p \) orbitals of sp\(^2\) hybridized B and N atoms. In the \( \alpha_2 \) and \( \beta_2 \) allotropes, \( p \) orbitals of all the atoms contribute to the CBM character.

We also observe an unusually flat band in the band structure of \( \alpha_2 \) and \( \beta_2 \) allotropes of BNP\(_2\) at the top of the valence region, along the \( \Gamma - X \) line. To further explore the origin of this flat band, we show 2D contour plots of the dispersion within the top valence and bottom conduction bands in Fig. 4.

In both allotropes, the CBM energy minimum occurs at the \( \Gamma \) point and the band dispersion around it is almost isotropic and free-electron like. In contrast, the VBM is displaced from the \( \Gamma \) point in the direction towards \( X \) for both allotropes. Whereas the band dispersion is almost flat along the \( x \)-direction, it is significantly higher along \( y \)-direction near the VBM, indicating a significant anisotropy in the carrier effective mass. As seen in Fig. 3(b) and (d), this is caused at the VBM by a larger separation and lower hybridization between the \( p \) lone pair states along the \( x \)-direction than along the \( y \)-direction.

### Electronic structure of BNP\(_2\) 2D allotropes

Results of our DFT calculations for the electronic structure of BNP\(_2\) monolayers are presented in Fig. 3. Our DFT-PBE results show all the four allotropes to be semiconductors. The fundamental band gap is direct in \( \alpha_1 \)-BNP\(_2\) and indirect in all the other BNP\(_2\) allotropes. Band gap values \( E_g \) based on DFT-PBE Kohn-Sham energies, ranging from 0.52 eV to 1.39 eV, are listed in Table I. We should note here that the interpretation of Kohn-Sham eigenvalues as self-energies is strictly incorrect and that DFT-based band gaps are typically underestimated. We find this to be the case when comparing band gap values based on DFT-PBE and the hybrid DFT-HSE06 functional in Table I. As seen when comparing band structure results based on DFT-PBE, given by the solid lines in Fig. 3, and DFT-HSE06, shown by the red dashed lines, the main difference is the opening of the fundamental band gap in DFT-HSE06, whereas the band dispersion is unaffected. We also present the total electronic density of states (DOS) and its projection onto the different species next to the band structure plots.

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### Electronic structure of C\(_2\)SiS 2D allotropes

Results of our DFT calculations for the electronic structure of C\(_2\)SiS monolayers are presented in Fig. 5.
FIG. 5. Electronic structure of a C$_2$SiS monolayer. The calculated band structure $E(k)$ and the density of states (DOS) including its projection on individual atoms are shown in the left panels. The partial charge density distributions at the valence band maximum (VBM) and the conduction band minimum (CBM) for the semiconducting allotropes and for the frontier states in the semimetallic allotropes are shown in the right panels. Results are presented for the (a) $\alpha_1$, (b) $\alpha_2$, (c) $\beta_1$, and (d) $\beta_2$ allotropes. All results are based on the DFT-PBE functional with the exception of DFT-HSE06 data, which are shown by the red dashed lines in the band structure plots. The blue arrows indicate the fundamental band gap in the semiconducting allotropes. Contributions of different atoms are distinguished by color in the PDOS plots. Isosurface plots of the partial charge density are presented at the isosurface value of $8.0 \times 10^{-3} e/\text{Bohr}^3$ for all allotropes.

Our findings indicate that only the $\alpha_1$ and the $\beta_1$ allotropes are semiconducting, whereas the $\alpha_2$ and $\beta_2$ allotropes are semimetallic. The band gap is indirect in $\alpha_1$-C$_2$SiS and direct in $\beta_1$-C$_2$SiS. Numerical band gap values based on DFT-PBE and DFT-HSE06 are listed in Table I and fall in the range of values found in BNP$_2$.

According to Fig. 5, the character of VBM and CBM states in the semiconducting allotropes $\alpha_1$ and $\beta_1$ is very similar. In analogy to results for BNP$_2$, the VBM of C$_2$SiS is dominated by lone-pair orbitals of Si atoms and the CBM contains mostly out-of-local-plane $p$ orbitals of C atoms.

The $\alpha_2$ and $\beta_2$ allotropes of C$_2$SiS are found to be semimetallic by both DFT-PBE and DFT-HSE06. Dirac “cones” are seen in the band structure in Fig. 5(b) and (d), with the Dirac point at $E_F$ located between $\Gamma$ and $Y$ in the Brillouin zone. The frontier states at $E_F$ are dominated by out-of-plane $p$ orbitals on C atoms.

The Dirac “cones” of $\alpha_2$- and $\beta_2$-C$_2$SiS are visualized in more detail in Fig. 6. The band dispersion in both allotropes is linear around $E_F$, but anisotropic. As seen in Fig. 6(c) and (d), the cross-section of the “cone” at $E < E_F$ or $E > E_F$ is not a circle, but rather an ellipse elongated in the $k_x$-direction. The higher steepness of the band dispersion along the $y$-direction near the Dirac point is a consequence of a stronger interaction between $C2p$ orbitals within zigzag chains of carbons, aligned with the $y$-direction. These C chains in $\alpha_2$-C$_2$SiS and $\beta_2$-C$_2$SiS are clearly visible in Figs. 1(g) and (h). Otherwise, these “cones” are very similar in Dirac point location, band dispersion and its anisotropy in both allotropes.

Carrier mobilities in semiconducting BNP$_2$ and C$_2$SiS 2D allotropes

Anisotropy in semiconducting BNP$_2$ and C$_2$SiS 2D allotropes is not only limited to the geometry, the elastic response and the electronic structure, but is also present in the carrier mobility. In absence of defects and external scattering centers, the mobility of carriers in 2D semiconductors is limited by acoustic phonons. We calculated the carrier mobilities of BNP$_2$ and C$_2$SiS 2D systems along the $x$- and $y$-direction using the deformation potential theory expression [11, 44, 45]

$$\mu = \frac{e\hbar c_i}{k_B m_i^* m_d E_{1i}^2}.$$ (2)
Here, \( i \) represents the Cartesian direction, with \( i = 1 \) standing for \( x \) and \( i = 2 \) for \( y \), and \( c \) is the carrier charge. \( e_{i i} \) is the 2D elastic modulus [43] along the direction \( i \), obtained from the strain energy curve in Fig. 2. \( T \) is the temperature, \( m_{i}^* \) is the effective mass along the \( i \)-direction, and \( m_{d} \) is the average effective mass given by \( m_{d} = (m_{x}^*m_{y}^*)^{1/2} \). The deformation potential \( E_{1i} \) along the \( i \)-direction is determined at the valence band maximum (VBM) for holes and the conduction band minimum (CBM) for electrons. It is defined by \( E_{1i} = \Delta V/(\Delta a_{i}/a_{i}) \), where \( \Delta V \) is the energy shift of the band edge with respect to the vacuum level under a small change \( \Delta a_{i} \) of the lattice constant \( a_{i} \). Our results for room-temperature carrier mobilities in all semiconducting 2D allotropes are summarized in Table II.

We found that most allotropes in our study exhibit very high and remarkably anisotropic carrier mobilities. The highest carrier mobility value we found is \( \mu_{y} = 1.51 \times 10^{5} \) cm$^{2}$/V$\cdot$s$^{-1}$ for electrons in \( \alpha_1 \)-BNP$_2$ along the \( y \)-direction, over two orders of magnitude higher than the value \( \mu_{x} = 0.4 \times 10^{3} \) cm$^{2}$/V$\cdot$s$^{-1}$ along the \( x \)-direction.

An important contributing factor to the mobility is the 2D elastic modulus [43]. The superior electron mobility along its \( y \)-direction is a result of increased stiffness along this direction. According to Table I, \( c_{22} \) is indeed much larger than \( c_{11} \) for most allotropes we study.

Unlike for electrons, hole mobility is highest along the \( x \)-direction in \( \beta_1 \), \( \alpha_2 \) and \( \beta_2 \) allotropes of BNP$_2$. The change of preferential transport direction is caused by substantial deformation potential anisotropy \( E_{1x} < E_{1y} \) at the VBM according to Table II. Carrier mobilities in semiconducting 2D allotropes of C$_2$SiS are comparable to those in BNP$_2$.

Carrier mobilities \( \mu > 10^{5} \) cm$^{2}$/V$\cdot$s$^{-1}$ in \( \alpha_1 \)-BNP$_2$ with \( E_{g} > 0.5 \) eV and \( \mu \geq 10^{4} \) cm$^{2}$/V$\cdot$s$^{-1}$ in \( \alpha_2 \) and \( \beta_2 \) allotropes of BNP$_2$ with \( E_{g} > 1 \) eV, evaluated at the PBE level of DFT are unusually high in view of the wide band gaps. This is particularly evident when compared to the values found in other similar 2D materials, as discussed in the Appendix. Even though these mobilities will be reduced due to inevitable defects and the interaction with the substrate under realistic conditions, we expect values in excess of \( \mu = 0.3 \times 10^{3} \) cm$^{2}$/V$\cdot$s$^{-1}$, which has been reported for phosphorene [6]. These results are very promising for the realization of 2D semiconducting

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**TABLE II. Calculated carrier mobilities and related quantities in semiconducting BNP$_2$ and C$_2$SiS allotropes.**

| Allotrope     | \( m_{x}^a \) \( (m_0) \) | \( m_{y}^a \) \( (m_0) \) | \( E_{1x}^b \) (eV) | \( E_{1y}^b \) (eV) | \( \mu_{x}^c \) \( (10^3 \) cm$^{2}$/V$\cdot$s$^{-1}$) | \( \mu_{y}^c \) \( (10^3 \) cm$^{2}$/V$\cdot$s$^{-1}$) |
|---------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \( \alpha_1 \)-BNP$_2$ | 0.51             | 0.34             | 1.36             | 0.40             | 0.40             | 151.21           |
|                | 0.75             | 0.39             | 1.83             | 1.60             | 0.11             | 6.16             |
| \( \beta_1 \)-BNP$_2$ | 0.67             | 0.34             | 0.69             | 1.37             | 5.89             | 10.51            |
|                | 0.67             | 0.57             | 0.37             | 1.26             | 15.82            | 5.62             |
| \( \alpha_2 \)-BNP$_2$ | 0.88             | 0.78             | 1.01             | 0.88             | 0.30             | 8.29             |
|                | 3.13             | 0.50             | 0.10             | 5.07             | 5.67             | 0.26             |
| \( \beta_2 \)-BNP$_2$ | 0.53             | 0.75             | 2.41             | 0.68             | 0.65             | 17.17            |
|                | 1.63             | 0.52             | 0.90             | 5.96             | 1.03             | 0.22             |
| \( \alpha_1 \)-C$_2$SiS | 0.53             | 0.28             | 0.39             | 1.37             | 4.38             | 15.66            |
|                | 1.72             | 0.76             | 2.54             | 0.87             | 0.01             | 4.85             |
| \( \beta_1 \)-C$_2$SiS | 0.14             | 1.57             | 2.51             | 6.31             | 1.69             | 0.09             |
|                | 0.78             | 2.24             | 1.87             | 1.42             | 0.20             | 0.45             |

Electrons are denoted by \( e \) and holes by \( h \).

\( a \) \( m_{x}^a \) \( (m_{y}^a) \) are the carrier effective masses along the \( x \) \((y)\) direction.

\( b \) \( E_{1x} \) \( (E_{1y}) \) are the deformation potentials along the \( x \) \((y)\) direction.

\( c \) \( \mu_{x} \) \( (\mu_{y}) \) are the carrier mobilities along the \( x \) \((y)\) direction at 300 K.
devices with high ON/OFF ratios and on-state currents.

SUMMARY AND CONCLUSIONS

In summary, we have introduced previously unexplored 2D ternary compounds BNP$_2$ and C$_2$SiS as isoelectronic counterparts of 2D PC structures. Using \textit{ab initio} density functional theory, we have identified four stable allotropes of each compound and confirmed their stability by calculated phonon spectra and molecular dynamics simulations. All allotropes display structural and elastic anisotropy due to structural ridges in their geometry, which are caused by coexisting $sp^2$ and $sp^3$ hybridization. Whereas all BNP$_2$ allotropes are semiconducting, we find only two allotropes of C$_2$SiS to be semiconducting. The other two allotropes of C$_2$SiS are semimetallic and show anisotropic Dirac cones at $E_F$. The fundamental band gaps of the semiconducting allotropes we study range from 0.5 eV to 1.4 eV at the PBE level and 1.4 eV to 2.2 eV at the HSE06 level of DFT. These 2D systems display carrier mobilities as high as $1.5 \times 10^5$ cm$^2$/V$^{-1}$s$^{-1}$. Such high mobilities, with two orders of magnitude in anisotropy ratio, are desirable, but quite uncommon in semiconductors with so wide band gaps. Combination of wide band gaps with high and anisotropic carrier mobilities offer great promise for applications of 2D BNP$_2$ and C$_2$SiS structures in electronics and optoelectronics.

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APPENDIX

Metastable structures of 2D BNP$_2$ and C$_2$SiS

As seen in Fig. 1 of the main text, $\alpha_1$ and $\beta_1$ allotropes of BNP$_2$ contain four polar B-N dimers aligned with the $x$-axis in each unit cell. Each of these dimer bonds may be rotated by $180^\circ$. This gives rise to four metastable structures for $\alpha_1$-BNP$_2$ and another four structures for $\beta_1$-BNP$_2$, shown in Fig. A1. The most stable structures among these, with the cohesive energy value highlighted in red, have been considered in the main text.

FIG. A1. Ball-and-stick model of metastable structures related to the $\alpha_1$ and $\beta_1$ allotropes of BNP$_2$, shown in top view. Cohesive energies $E_{coh}$ are presented below each structure, with the value for the most stable configuration highlighted in red.

FIG. A2. Ball-and-stick model of metastable structures related to the $\alpha_1$ and $\beta_1$ allotropes of C$_2$SiS, shown in top view. Cohesive energies $E_{coh}$ are presented below each structure, with the value for the most stable configuration highlighted in red.

FIG. A3. Ball-and-stick model of metastable structures related to the $\alpha_2$ and $\beta_2$ allotropes of BNP$_2$, shown in top view. Cohesive energies $E_{coh}$ are presented below each structure, with the value for the most stable configuration highlighted in red.
Quite different is the arrangement of B and N atoms in zigzag chains in the \( \alpha_2 \) and \( \beta_2 \) allotropes of BNP\(_2\) shown in Fig. 1 of the main text. Also in this case, each bond may be rotated by 180°. This gives rise to two metastable structures for \( \alpha_2\)-BNP\(_2\) and another two structures for \( \beta_2\)-BNP\(_2\), shown in Fig. A2. Only the most stable among these allotropes have been considered in the main text.

Next we turn to the \( \alpha_1 \) and \( \beta_1 \) allotropes of C\(_2\)SiS, displayed in Fig. 1(e) and (f) of the main text. Unlike in BNP\(_2\), we can find only three inequivalent metastable
structures for these systems, displayed in Fig. A3. For the \( \alpha_2 \) and \( \beta_2 \) allotropes of \( \text{C}_2\text{SiS} \), optimization leads to only one stable structure. As for the other systems discussed above, we only consider only the most stable allotropes in the main text.

**Phonon spectra of 2D BNP\(_2\) and C\(_2\)SiS allotropes**

A real confirmation of structural stability, more important than a high cohesive energy, comes from the phonon spectra. Structures can be considered stable if no imaginary frequencies can be found in the phonon spectra.
The calculated phonon spectra of all BNP$_2$ and C$_2$SiS allotropes discussed in this study are displayed in Fig. A4. We should note at this point that phonon calculations for 2D structures with the uniquely soft flexural ZA mode are very demanding on precision [46]. We found our phonon spectra to be essentially free of imaginary frequencies associated with decay modes. The highest imaginary frequency value $\omega \lesssim 127$ cm$^{-1}$ in our spectra belongs to the ZA mode near the $\Gamma$ point in the Brillouin zone and is an artifact related to numerical precision [46].

**Thermodynamic stability of 2D BNP$_2$ and C$_2$SiS allotropes**

Whereas phonon spectra tell about structural stability in the harmonic regime, they cannot determine if a structure will or will not fall apart at a given finite temperature. To study the thermodynamic stability of the ternary structures in this study, we performed a set of ab initio canonical molecular dynamics (MD) simulations at 300 K, 500 K and 1000 K and present our results in Fig. A5 for 2D BNP$_2$ and Fig. A6 for C$_2$SiS structures. For 15 ps long MD runs, we plotted both the fluctuations of the total potential energy and snapshots of the structures after 15 ps.

Our results in Fig. A5 indicate that all four allotropes of BNP$_2$ maintained their geometries up 1000 K, indicating a high thermodynamic stability. The corresponding results for C$_2$SiS in Fig. A6 indicate all allotropes to be stable at 300 K and 500 K. Further increase of temperature to 1000 K causes a dramatic degradation of the $\alpha_1$ and $\beta_1$ allotropes of C$_2$SiS after 3 ps. The $\alpha_2$ and $\beta_2$ allotropes appear more stable at 1000 K, but their significant distortion indicates onset of degradation. The thermodynamic stability of all the BNP$_2$ and C$_2$SiS allotropes is either comparable to or superior to other similar 2D structures including GeP$_3$ [16], which was shown to be stable at $T \lesssim 500$ K, as well as PC [11] and binary V-V compounds [47], which were shown to be stable only up to $\approx 300$ K. Our MD results show good consistency with the conclusions obtained from the formation energy calculations discussed in the main text.

**Suitability of BNP$_2$ and C$_2$SiS allotropes for electronic applications**

Combination of high carrier mobility and wide band gap is very desirable, as it results in a high ON/OFF ratio and a high on-state current in semiconductor devices. The 2D materials we introduce appear particularly suitable for electronic applications from that viewpoint. This is evidenced in Fig. A7, where we compare mobilities and band gaps of BNP$_2$ and C$_2$SiS to those of 2D-PC, GeP$_3$ [16], SnP$_3$ [17], black phosphorene, and 2D GeSe [48]. There is a general trade-off relation between carrier mobility and band gap. We find most of the BNP$_2$ and C$_2$SiS allotropes to be near the upper limit of the trade-off.

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